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A computer model has been developed to simulate the fate and transport of heavy metals introduced to a wetland ecosystem. Modeled water quality variables include plankton biomass and productivity; macrophyte (*Nelumbo lutea*) biomass; total phosphorus in the water column; dissolved copper in the water column and sediments; particulate copper in the water column and sediments; and suspended solids. These variables directly affect the modeled rate of copper uptake by macrophytes, and the rate of copper recycling as a function of the decomposition of copper-laden biomass litter.

The model was calibrated using total phosphorus and chlorophyll-*a* data from the Old Woman Creek Wetland in Ohio. Verification of the model was achieved using data on the copper content of the macrophyte *Nelumbo lutea*. The effects of harvesting copper-laden biomass on the longevity of the wetland ecosystem were also evaluated.

# MODELING HEAVY METAL REMOVAL IN WETLANDS

A Thesis Presented to the  
Faculty of the School of Engineering and Applied Science  
University of Virginia

In Partial Fulfillment  
of the Requirements for the Degree  
Master of Science (Civil Engineering)

by

Ronald N. Light

May 1992

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## ABSTRACT

Although the use of wetland ecosystems to purify water has gained increased attention only recently, it has been recognized as a wastewater purification technique for centuries. While considerable research has occurred to quantify the nutrient (nitrogen and phosphorus) removal mechanisms of wetlands, relatively few investigators have focused on the mechanisms of heavy metal removal and uptake by wetland sediments and plants. The quantification of the assimilative capacity of heavy metals by wetland ecosystems is a critical component in the design and use of wetlands for this purpose.

A computer model has been developed to simulate the fate and transport of heavy metals introduced to a wetland ecosystem. Modeled water quality variables include plankton biomass and productivity; macrophyte (*Nelumbo lutea*) biomass; total phosphorus in the water column; dissolved copper in the water column and sediments; particulate copper in the water column and sediments; and suspended solids. These variables directly affect the modeled rate of copper uptake by macrophytes, and the rate of copper recycling as a function of the decomposition of copper-laden biomass litter.

The model was calibrated using total phosphorus and chlorophyll-*a* data from the Old Woman Creek Wetland in Ohio. Verification of the model was achieved using data on the copper content of the macrophyte *Nelumbo lutea*. The effects of harvesting copper-laden biomass on the longevity of the wetland ecosystem were also evaluated.

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## 1. INTRODUCTION

Upon the passage of the 1972 Clean Water Act, the Environmental Protection Agency (EPA) has regulated point source discharges of pollutants to waters of the United States through the National Pollutant Discharge Permit System (NPDES). In recent years, the EPA has extended permitting to pollutants discharged from stormwater, as well. Within the framework of these regulations, industries, municipalities, and cities have sought economical methods to treat pollutant discharges.

Heavy metals, such as lead, nickel, zinc, cadmium, mercury, and copper are a potentially toxic component of many wastewater effluents. Once thought to be limited to acid mine drainage and industrial wastewater, heavy metals are now recognized as a significant, sometimes lethal component of municipal wastewater. In its 1982 publication entitled "Fate of Priority Pollutants in Publicly Owned Treatment Works (POTWs)" (EPA, 1982), the EPA released the results of its study of the fate and occurrence of 129 priority pollutants in 50 POTWs. Among the key findings of this study was that 12 of the 16 most commonly occurring pollutants were *metals*.

In the EPA study, copper, lead, nickel, zinc, and cadmium, among others, were detected in 100% of the wastewater samples tested (Fricke *et al.*, 1985). Stormwater runoff from heavily urbanized areas is typically high in heavy metal content as well. Treatment of heavy metal-laden wastewater effluents, therefore, is an important aspect of wastewater treatment.

The use of natural and artificial (i.e., man-made) *wetlands* to treat heavy metal-laden effluents, once limited to acid mine drainage effluents, has continued to gain acceptance as a low-cost, relatively safe way to treat this component of a broad range of industrial and municipal effluents, and stormwater runoff. In a report prepared for the EPA Risk Reduction Engineering Laboratory, Reed (1991) identified 154 wetlands constructed to treat wastewater, indicative of the increased use of this method of wastewater treatment in the United States.

When used as an effluent treatment system, wetlands function in much the same way as a facultative wastewater treatment pond (Peavy *et al.*, 1985). Macrophytic and microphytic plants convert organic wastewater constituents into harmless byproducts in an aerobic zone (water column); microorganisms convert these organics in an anaerobic zone (sediments). Nitrogen and phosphorus are used as nutrients, assimilated into plant biomass, and released back into the wetland system upon plant death. Much of the available nutrient pool settles to sediments, where it becomes relatively immobile.

Inorganic wastewater constituents, such as heavy metals, are assimilated and released in much the same way. In small amounts (ppm to ppb), heavy metals application will not adversely affect the wetland system's ability to purify or polish wastewater effluents. In fact, several heavy metals are considered micronutrients, and wetland systems are often deficient in one or more of these substances (Hodgson, 1963; Barber, 1984). However, beyond certain limits heavy metals become toxic to macrophytic and microphytic plants; when toxicity occurs, the wetland may

cease functioning as a treatment system.

Thus, research which characterizes the removal pathways of heavy metals, and the ultimate fate of heavy metals in a wetland managed for wastewater treatment, can identify potential hazardous heavy metal loadings and be the basis for decisions regarding effluent pretreatment to remove high or toxic levels of heavy metals before discharge into a wetland treatment system. Knowledge of the heavy metal assimilative capacity of wetland plants can serve as a valuable tool to adjust the concentrations of these substances applied to wetlands, and can also indicate when biomass harvesting is desirable to extend the life of the wetland system for wastewater treatment purposes. The need for this information is the basis for the development of a wetland heavy metal removal model.

This thesis work consists of the development of a fate and transport computer model to follow the heavy metal copper as it is introduced into a wetland ecosystem. Within the typical wetland system, copper exists in several forms in the dissolved metal pool; in macrophytic and microphytic plants, and their lysed cell mass or litter; and in sediments. Thus, the key physical processes considered in the model are dispersion and advection; sedimentation and resuspension; adsorption and desorption; and metal speciation.

The computer model was based on data from the Old Woman Creek Wetland, located in northern Ohio. Frizado *et al.* (1986), Klarer (1988), Mitsch (1989), and Mitsch and Reeder (1991), among others, have studied this system extensively, and therefore a wealth of data exists with which the model presented here was calibrated

and verified.

### 1.1 Copper as a Micronutrient

Several heavy metals have long been considered as micronutrients in both upland and wetland soils, although the range between acceptable and toxic levels is variable (Patrick *et al.*, 1985). Some copper exists naturally in the environment. Hodgson (1963) reported copper concentrations in the earth's crust, sedimentary rocks, and soils as 45-70 ppm, 57 ppm, and 20 ppm, respectively. He and Barber (1984) reported that organic soils are most typically deficient in micronutrients; copper additions of 50-200 pounds per acre to improve fertility are common in muck, wetland-type soils as reported by Hodgson.

In flooded, wetland soils, factors which contribute to micronutrient deficiencies may include low micronutrient soil composition; high soil pH; high organic matter (Barber, 1984); and micronutrient interactions (Patrick *et al.*, 1985). The range between beneficial and toxic concentrations of copper, however, is quite variable.

Cowgill (1970) studied copper in macrophytic plants at a site in Connecticut, and reported copper concentrations in three macrophytes (as a per cent) as 0.0333 (*Salix nigra* L.), 0.0362 (*Pyrus malus* L.), and 0.0062 (*Lemna minor* L.); Cowgill cited a mean copper concentration (as a per cent) for vegetation as 0.00027. For two study years, the range of copper concentrations (dry weight basis) in submerged water plants was 32.3-52.4 ppm (mean, 46.2 ppm, 1971 data), and 24.5-47.7 ppm (mean 36.0

ppm, 1972 data).

Other copper concentration data cited by Cowgill (1974) indicate macrophytic copper concentrations from 2.5 to 370.0 ppm. Cowgill's results led her to conclude that the amount of copper in plants is "highly variable", but that the concentration of copper in aquatic plants "appears to bracket" copper concentrations found in terrestrial plants (Cowgill, 1974).

Work by Boyd (1970) to analyze the chemical composition of aquatic plants (by dry weight) revealed that submersed species ranged from  $30 \pm 7$  ppm to  $48 \pm 9$  ppm; floating leafed plants ranged from  $32 \pm 5$  ppm to  $40 \pm 7$  ppm; and emergent species ranged from 20 to 60 ppm. Boyd reported copper concentrations in *Nelumbo lutea* (the dominant macrophyte in the Old Woman Creek Wetland) as  $40 \pm 7$  ppm.

Later work by Boyd (1978) found an average copper concentration of  $40 \pm 6$  ppm in a total of 33 species of aquatic macrophytes, while the concentration range varied from 1 to 190 ppm. Boyd's results suggest that while uptake of copper by plants may be relatively low, storage of copper may reach high levels.

While Boyd showed the potential for macrophytes to translocate copper from the environment, he cautioned against applying a "typical" copper concentration to macrophytic plants, arguing that copper uptake is both species and location specific (the same caveat was echoed in a later study by Taylor and Crowder (1983)).

This specificity has limited the general use of macrophytes as a "pump" to remove copper introduced to a wetland; the lack of a typical stoichiometric relation between copper and other nutrients, such as exists for nitrogen and phosphorus, has also

slowed the use of wetland plants as a heavy metal treatment media. Interestingly, Boyd found that copper, manganese, and phosphorus concentrations were similar for floating, emergent, and submersed plants.

The toxicity of copper to aquatic plants is a concern in wetland systems used for wastewater treatment. Research on toxicity is also variable. Moore and Ramamoorthy (1984) indicate that inhibition of growth to most aquatic plants generally occurs at concentrations of copper  $\leq 0.1$  mg/L in solution. Brown and Rattigan (1979), however, found that copper toxicity to *Elodea Canadensis* occurred at a copper concentration of about 3 mg/L after 4 weeks.

Available research has demonstrated that among the typical heavy metals in municipal wastewater, copper may potentially be the most deleterious to wetlands. With the exception of mercury, copper is the most consistently toxic to aquatic plants (Brown and Rattigan, 1979; Moore and Ramamoorthy, 1984). Of copper, mercury, arsenic, cadmium, lead, and zinc, copper produced the highest toxicity to fully-submerged (*Elodea canadensis*) and partially submerged (*Myriophyllum spicatum*) aquatic macrophytes (Brown and Rattigan, 1979).

In the same study, Brown and Rattigan evaluated the effect of dissolved metals on the photosynthetic oxygen evolution of *Elodea canadensis*, and found copper reduced photosynthetic oxygen evolution by 50% at .15 mg/L, the lowest concentration of 9 metals tested except for silver (.10 mg/L). In a study of copper and lead removal using a "thin-film nutrient" technique by aquatic macrophytes, copper was found to be the metal responsible for system failure and plant toxicity

(Dierberg *et al.*, 1986).

Taylor *et al.*, (1990) modeled the phytotoxicity to *Triticum aestivum* of six heavy metals, including copper, using the Weibull frequency distribution. Taylor found that after cadmium, copper was most toxic; the Weibull frequency distribution produced good estimates of maximum growth, minimum growth, growth response, toxicity threshold, and maximum unit toxicity for the metals studied. Copper toxicity was found to be at levels above 3.4  $\mu\text{mol/L}$  (.216 mg/L); a 19% growth reduction per  $\mu\text{mol/L}$  was estimated.

Lidon and Henriques (1991) investigated the effects on the photosynthetic processes of rice plants at copper concentrations from .002 to 6.25 mg/L, at a pH held at about 5.5, suggesting that the copper available to the plants was free  $\text{Cu}^{2+}$  (Sylva, 1976). In this study, which found that rice plants have an internal copper regulating mechanism which controls the amount of copper translocated from the root to the shoot, a "below normal" (deficient) level of copper in solution was considered to be .002 mg/L; "normal" was considered to be 0.01 mg/L; and "toxic" levels of copper in solution were considered to be above .05 mg/L (Lidon and Henriques, 1991).

Lidon and Henriques subjected rice plants to a number of copper solution regimes. Toxic effects to plants were assessed at 0.05, .25, 1.25, and 6.25 mg/L. Above 1.25 mg/L, the internal copper regulating mechanism of the rice plants appeared to fail, allowing excessive copper to be transferred from the roots to the shoots, thereby causing toxicity. The range of copper concentrations in rice shoot



tissues at various copper treatments appears in Table 1.1, on the following page.

It is important to note, however, that the toxicity threshold suggested by Lidon and Henriques cannot be immediately applied to natural systems, where the pH is typically higher and copper may undergo complexation. Plant copper toxicity may therefore be "buffered" in natural systems where high pH and complexation conditions occur.

It is clear from Table 1.1 (following page) that copper concentrations in plants is dependent on the level of copper available to the plant, and that even at high concentrations of copper in solution, the plant may continue to adsorb copper, until photosynthesis is inhibited. It is also interesting to note that at copper concentrations between .05 and .25 mg/L, copper concentration bracketed the average value of 40  $\mu\text{g/g}$  cited by Boyd (1978), above.

Thus, as it appears to be toxic at low concentrations and relatively more toxic than other heavy metals of interest, this study focused on the mechanisms of *copper* removal in wetlands. The selection of copper as the heavy metal of interest is further supported by Rendig and Taylor (1989), who note that uptake of copper by plants is the least of the heavy metals. The ability of plants to continue to remove copper (that is, at concentrations below an acute toxicity threshold), therefore, may also tend to indicate continued uptake of other heavy metals as well.

Table 1.1

Concentrations of Copper in Rice Plants at Various Copper Treatments

Copper Treatments (mg Cu/L)	Copper Concentration in Rice Plants $\mu\text{g/g}$ dry weight $\pm$ (S.E.)
0.002	17.5 $\pm$ 1.2
0.01	21.5 $\pm$ 1.6
0.05	27.0 $\pm$ 2.1
0.25	46.5 $\pm$ 3.3
1.25	95.0 $\pm$ 6.9
6.25	508.0 $\pm$ 21.1

Source: Lidon and Henriques, 1991

In addition to the effect of heavy metals on macrophytic plants, certain heavy metals have been shown to be toxic to nitrifying bacteria, upon which the removal of nitrogen in a wetland rests (Watson *et al.*, 1989), and mosquito-controlling fish (Wieder *et al.*, 1989). Other concerns focus on the biouptake of heavy metals by other aquatic life, including migratory waterfowl, mussels, and crabs (Giblin *et al.*, 1980).

To address the need to predict copper uptake by wetland plants at various copper concentrations, this work has developed a model framework which is easily modified based on site specific wetland conditions. The focus of this modeling effort has been

to quantify the removal mechanisms of copper-laden effluents by wetland systems to predict the relative removal roles of sediments and macrophytic plants. The effects of copper on wetland faunal systems has been left to others in order to limit the scope of the present modeling effort.

## 2. PREVIOUS WORK

Although the use of wetland ecosystems to purify water has gained increased attention only recently (within the past 20 years), it has been recognized as a wastewater purification technique for centuries (Heliotis and DeWitt, 1983). Considerable research has occurred to quantify the nutrient removal mechanisms of wetlands.

### 2.1 Work in Nutrient Removal in Wetlands

Work to assess the wastewater purification potential of constructed wetlands began in the 1950s by Seidel (1976). Since then, a first step in effective research has considered wetland hydrology as a key component in the phenomenon of nutrient removal (Howard-Williams, 1985; Mitsch and Reeder, 1991), and much work has occurred in this field (Petryk and Bosmajian, 1975; Kadlec *et al.*, 1981; Hammer and Kadlec, 1986; and Kadlec, 1990). The mechanisms of hydrology control the flow into and out of wetland systems, and thereby control the transport of particulate and dissolved nutrients (Kadlec, 1983). Within the framework of the hydrologic system, dilution and retention time of wastewater effluents in the wetland system are recognized as important processes in the removal of nutrients.

As a nutrient-laden effluent moves into a wetland and dissipates, some of the pollutant load is reduced by filtering and settling. Microorganisms attached to

emergent vegetation provide further removal, much like the action of a trickling filter (Nichols, 1983; Howard-Williams, 1985).

While early research attempted to quantify nutrient removal using the "black box" approach, the principles of mass balance are applied successfully today. The nutrients of primary interest include nitrogen and phosphorus. Within wetland systems, nutrient cycling is complex, especially in the case of nitrogen. The major elements of the nitrogen and phosphorus cycle follow.

The assimilative capacity of wetland systems to store phosphorus is typically small, related to the relatively simple cycling of phosphorus between microphytic and macrophytic plants, water column, and sediments, and a "breakthrough" of phosphorus in the outflow of wetland systems used for nutrient removal often occurs (Kadlec, 1983; Richardson, 1985). Adsorption, precipitation, and resuspension are considered the dominant physical processes which affect phosphorus dynamics in wetland systems (Nichols, 1983). Reductions in total phosphorus in wetland systems are quite variable and range from 37-61% (Finlayson and Chick, 1983), to between 20-96% (Nichols, 1983).

Compared to phosphorus, the nutrient cycle for nitrogen is far more complex. Major components of the nitrogen cycling system include denitrification, uptake by microphytic and macrophytic plants, deposition to sediments, and limited volatilization of  $\text{NH}_3$  to the atmosphere (Nichols, 1983; Howard-Williams, 1985). Of these, loss of nitrogen to organic-rich wetland sediments is considered to be the dominant removal pathway. Reports of nitrogen uptake rates are also considerably

variable. Nichols (1983) reported total nitrogen removal values from 1-96% under several conditions; Finlayson and Chick (1983) cited total nitrogen removal rates of 14-56%, while 93% removal was reported by Knight *et al.*, (1985).

## **2.2 Work in Heavy Metals Removal in Wetlands**

Most studies which have investigated the use of wetlands to treat heavy metal-laden wastewater have focused on acid mine drainage (Wildeman and Laudon, 1988; Hammer, 1989). The lack of information on the fate and effects of heavy metals in wetlands has slowed the use of wetlands to treat heavy metal-laden effluent. Since the level of heavy metals in a wetland can limit its wastewater purification ability (that is, through toxicity to wetland flora, shown to be important in nutrient removal), characterization of heavy metal removal mechanisms in wetlands is important.

Research conducted to determine the fate of heavy metals in a wetland used for wastewater treatment has generally focused on the uptake of heavy metals by microphytic and/or macrophytic plants, however sedimentation, and precipitation are also recognized as key removal mechanisms (Cooley *et al.*, 1979; Taylor and Crowder, 1983; Heliotis and DeWitt, 1983; Valdares *et al.*, 1983; Pip, 1990; and Zolotukhina and Gavrilenko, 1990).

Simpson *et al.* (1983), found that vegetation played a "major role" in Cu, Pb, and Ni removal in a wetland, and that dead biomass (litter) acted as a temporary storage medium for these and other heavy metals. Simpson's work is supported by earlier

studies by Davis and van der Valk (1978), and Odum and Heywood (1978) on the decomposition of freshwater wetland plants.

Tuschall (1981) found that heavy metals were immobilized in wetlands by predominantly 3 factors: levels of dissolved inorganic carbon, iron, and calcium. Tuschall calculated immobilization rates for Cd, Cu, Mn, and Zn; values ranged from 7.2 to 72 grams/metal per hectare per day.

However, while researchers have shown rates of heavy metal uptake for various metals, few studies to date have examined the long term (>14-60 days) effects of heavy metal application to wetlands (Dierberg *et al.*, 1986). Beyond acute toxicity, the long term effects of heavy metal application to wetlands is not known at this time.

### **2.3 Previous Modeling Efforts**

Computer modeling represents an excellent method to describe this long-term phenomenon. It is especially useful until the chronic effects of heavy metal uptake by plants in wetland systems is known, as computer simulation provides a way to avoid potential damage to these ecosystems.

However, while substantial effort has been devoted to modeling nutrient removal (Claassen and Barber, 1976; Barber, 1984; Jorgensen, 1988; Kadlec and Hammer, 1988; Breen, 1990; and Mitsch and Reeder, 1991), and wetland hydrology (Petryk and Bosmajian, 1975; Kadlec *et al.*, 1981; Hammer and Kadlec, 1986; and Kadlec,

1990), relatively little work has occurred to simulate heavy metal removal in wetland systems.

Early work by Nielsen (1976 a,b,c) and Pettersson (1976) treated heavy metals uptake according to Michaelis-Menten kinetics (Lehninger, 1975), discussed later in detail.

While a number of models exist which allow simulation of the fate and transport of heavy metals, such as TOXIWASP (Ambrose *et al.*, 1983), and HSPF (Johanson *et al.*, 1984), no models are currently available which combine heavy metal fate and transport (Bonds, 1992), and uptake by aquatic plants. Even MINTEQA2, a powerful metals speciation model (Allison *et al.*, 1990), is limited in its ability to model all three principal components of the model presented here: transport, metal speciation, and uptake by aquatic plants. However, MINTEQA2 is incorporated in the model presented here to perform metals speciation calculations.



### 3. THE WETLAND SYSTEM AND THE AVAILABILITY OF DATA

The Old Woman Creek Wetland is part of the Old Woman Creek National Estuarine Sanctuary and State Nature Preserve, located along the banks of Lake Erie in northern Ohio (Figure 3.1). This site has been preserved as a research and study area (Figure 3.2); researchers have collected a significant amount of data which makes this site amenable for the current study.

#### 3.1 Old Woman Creek Wetland

The Old Woman Creek Wetland is 56 ha in size, about .34 km at its widest point, and varies in depth from .5 meters to 3 meters (Klarer, 1989). According to Mitsch and Reeder (1991), the predominant macrophytic flora in the wetland is American lotus (*Nelumbo lutea*); smaller stands of white waterlilies (*Nymphaea tuberosa*), spatterdock (*Nuphar advena*), arrow arum (*Peltandra virginica*), and cattails (*Typha* spp.) also occur.

The dominant macrophyte *Nelumbo lutea* occupied about 1/3 of the surface area of the wetland in 1988, the year for which significant data is available on other wetland parameters; according to Reeder (1992), this floating leafed species drifts about the wetland in large mats. Based on this observation, copper uptake by *Nelumbo* was considered to occur predominantly from the dissolved copper pool in the water column, rather than the sediments.

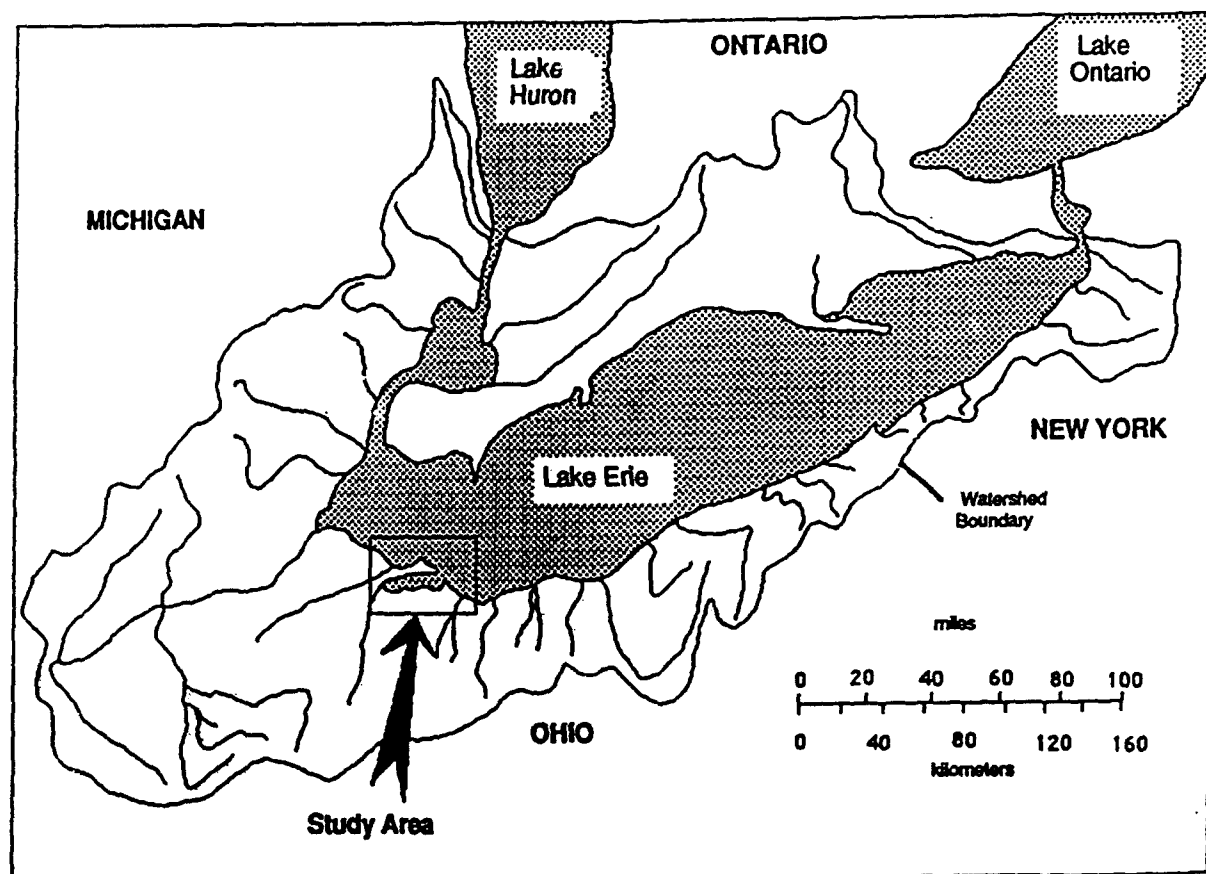


Figure 3.1: Map of the Study Area (Mitsch, 1989)

Old Woman Creek is the principal water source for the wetland system. The creek receives nonpoint source agricultural runoff and secondary sewage effluent from the town of Berlin Heights (population 800) (Mitsch and Reeder, 1991). The wetland was recently modeled using extensive data from 1988 (Mitsch, 1989; Mitsch and Reeder, 1991); data used by these and other researchers (Frizado, *et al* 1986; Baker, 1988; Klarer, *personal communication*, 1992; and Reeder, *personal communication*, 1992) were used for the current modeling effort. The pH of the wetland varied somewhat during the study period, ranging between 6.9 and 8.57. The pH of the sediments remained relatively constant at about 8.05.

The Old Woman Creek Wetland is separated from Lake Erie by a sand, barrier dune. When the dune is open, water flows out of the wetland, and some water may flow into the wetland from Lake Erie. During 1988 the area underwent a drought, and the barrier dune remained closed for most of the year (Mitsch and Reeder, 1991). The dune was open for 110 days, or about 30% of the year, during the period 3 January-15 May 1988. The dune was closed for 256 days in 1988, generally after 15 May (Herdendorf and Hume, 1991). Little or no outflow occurred from the wetland after about 15 May 1988 (Mitsch and Reeder, 1991). Based on this information, the wetland volume and depth were considered constant for the purposes of the current modeling effort.

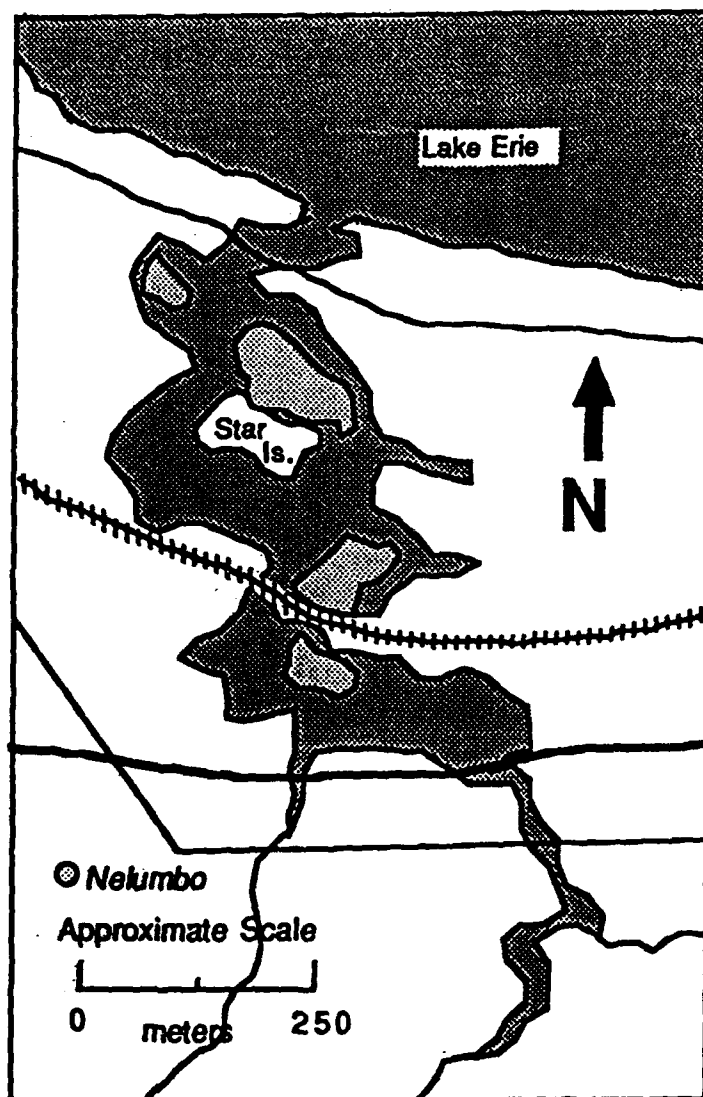


Figure 3.2: Map of the Old Woman Creek Wetland, Showing *Nelumbo lutea* Beds (Mitsch, 1989)

### 3.2 Copper Data

Following early work to characterize metal uptake by upland plants (Pettersson, 1976; Nielsen, 1976 a,b,c), additional work quantified copper uptake in microphytic and macrophytic plants (Cooley *et al.*, 1979; Taylor and Crowder, 1983; Simpson *et al.*, 1983; Kurihara and Suzuki, 1987; Dierberg *et al.*, 1987; Pip, 1990; and Zolotukhina and Gavrilenko, 1990). These data were used as a guide in assessing the results of the current modeling effort.

Extensive copper data were available from a 1986 NOAA Report entitled *Depositional and Diagenetic Processes in a Freshwater Estuary* (Frizado *et al.*, 1986), which contains copper data for the water column, sediments, interstitial root zone, and other compartments for the Old Woman Creek Wetland. However, only limited data were available on the copper concentration of *Nelumbo lutea*, and copper concentrations in neither the sediments nor water column were measured at the same time as *Nelumbo lutea* were harvested (Reeder, 1992, *personal communication*).

#### 4. DESCRIPTION OF MODEL KINETICS

The fundamental goal of this research was the development of a computer model to serve as a predictive tool for the management of heavy metal-laden effluent applications to wetland systems used for wastewater treatment. As heavy metals exist almost universally in municipal wastewater effluent (Fricke *et al.*, 1985), this study is applicable to the treatment of copper-laden wastewater typical of *municipal sources*.

Furthermore, although the study area is a natural wetland, many researchers have argued that the use of natural wetland ecosystems to treat wastewater should be avoided until the full effects of this practice are understood; the developed model is applicable for use in either natural or artificial wetland ecosystems.

This work has focused on several of the key issues regarding the ability of wetland systems to remove heavy metals, including: the characterization of copper removal by wetland sediments; the uptake of copper by aquatic plants through their root systems; the effect of biomass recycling on copper removal; and the effect of biomass harvesting on copper removal. Thus, three principal compartments for metal storage in a typical wetland ecosystem were characterized: sediments, live biomass, and dead biomass (litter).

A simplified version of the wetland ecosystem model appears at Figure 4.1, and considers the relationship between the water quality constituents modeled here: microphytic and macrophytic biomass; total phosphorus; dissolved and particulate

copper; copper uptake by macrophytes; and suspended solids.

### Modeling the Fate of Copper in a Wetland

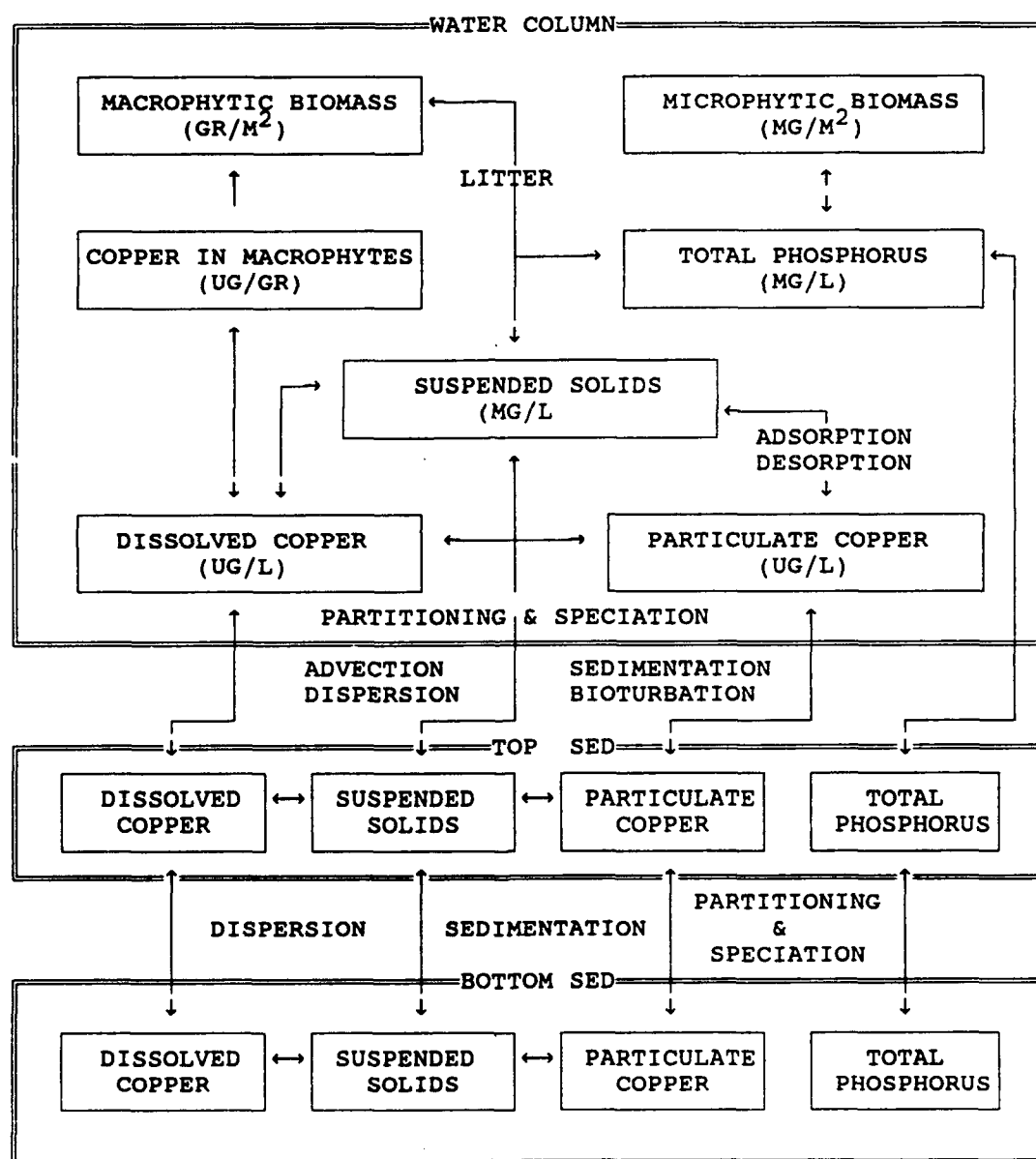


Figure 4.1

## Computer Simulation Framework

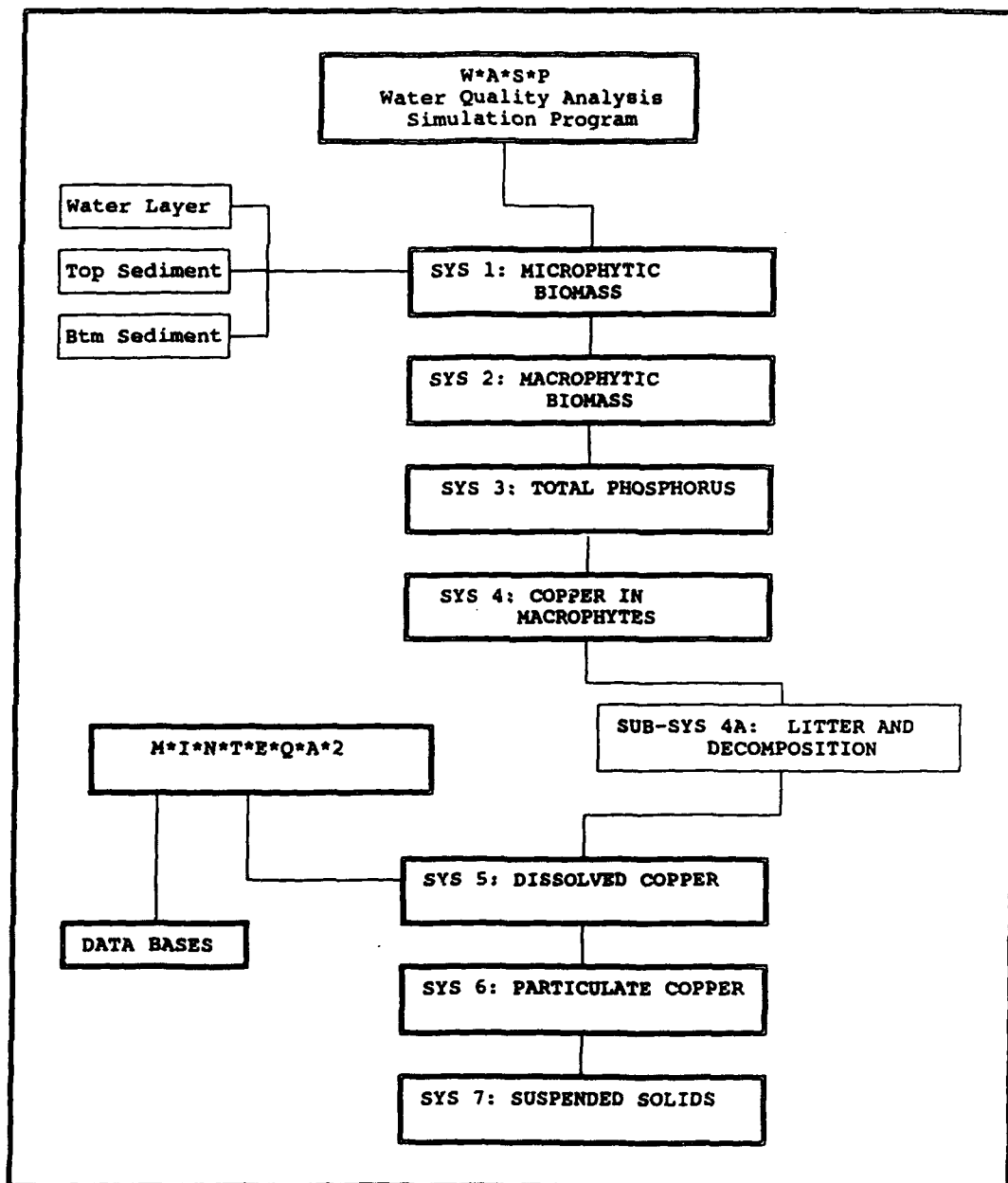


Figure 4.2



Figure 4.2, on the previous page, details the computer model simulation framework. The effect of litter kinetics on the concentration of copper in the wetland were assessed within the framework of these constituents, as shown.

The model reported here incorporated this framework into the computer simulation code WASP (DiToro *et al.* 1983), which served as the mechanism for calculating hydrodynamic transport data, and WASPB, the user-specified kinetics simulation code for the remaining submodels. MINTEQA2, a powerful metals speciation model, was included as a submodel to characterize the fate of copper in the wetland system. Following a brief discussion of the box model approach to mass balance calculations in Section 4.1, each kinetic subroutine is discussed.

#### **4.1 Mass Transport in the Box Model Approach**

The finite segment or box model approach is applicable to the solution of mass balance problems in a completely mixed, steady state system such as the wetland under consideration here (Thomann and Mueller, 1987). The current system is divided into three segments: one water column, a top sediment layer, and a bottom sediment layer. The Water Quality Analysis Simulation Program, WASP, calculates a mass balance around each water quality variable considered in each of these three interconnected, completely mixed segments.

The basic equation to formulate a mass balance for a constituent around segment  $k$  follows, after Bonds and Lung (1991).

$$V_k \frac{dC_{mk}}{dt} = 0 = \sum [ -Q_{kj} (\alpha_{kj} C_{mk} + \beta_{kj} C_{mj}) + E_{1kj} (C_{mj} - C_{mk}) ] - V_k K_{mnk} C_{mk} + W_{mk} \quad (1)$$

where:

$C_{mk}$  = concentration of water quality parameter  $m$  in segment  $k$ ,  $[M/L^3]$

$V_k$  = volume of segment  $k$ ,  $[L^3]$

$Q_{kj}$  = advective flow from segment  $k$  to segment  $j$ ,  $[L^3/T]$

$\alpha_{kj}$  = finite difference weight, function of the ratio of flow to dispersion,  $0 < \alpha < 1$

$\beta_{kj} = 1 - \alpha_{kj}$

$E_{1kj}$  = dispersive (exchange) flow between segments  $k$  and  $j$ ,  $[L^3/T] = E_{kj} A_{kj} / L_{avekj}$

$E_{kj}$  = dispersion coefficient between segments  $k$  and  $j$ ,  $[L^2/T]$

$A_{kj}$  = cross-sectional area between segments  $k$  and  $j$ ,  $[L^2]$

$L_{avekj}$  = average of characteristic lengths of segments  $k$  and  $j$ ,  $[L] = (L_k + L_j)/2$

$L_k$  = characteristic length of segment  $k$ ,  $[L]$

$K_{mnk}$  = first-order reaction coefficient in segment  $k$  for interaction of water quality parameter  $m$  with parameter  $n$ ,  $[1/T]$

$W_{mk}$  = source or sink of parameter  $m$  in segment  $k$ ,  $[M/T]$

and where  $M$ ,  $L$ , and  $T$  are the mass, length, and time units, respectively.

The first term on the right hand side of Equation 1 represents the mass of the water quality variable entering or leaving the segment  $k$  due to advective flow. The second term represents dispersion or mixing of the variable. The third term represents any first-order decay of the water quality variable; the last term represents sources and sinks of the variable (Bonds and Lung, 1991).

#### 4.2 Microphytic Gross Primary Productivity

The equation used to describe microphytic gross primary productivity, formulated after Mitsch and Reeder (1991) is as follows:

$$\frac{dC_1}{dt} = k_2 IAV - k_3 C_1 - s_p C_1 - k_1 C_1 \quad (2)$$

where:

$C_1$  = plankton biomass (kcal m<sup>2</sup>)

$k_1$  = outflow coefficient (day<sup>-1</sup>)

$k_2$  = gross primary productivity coefficient for microphytes, unitless

$IAV$  = time variable solar radiation (kcal m<sup>2</sup> day<sup>-1</sup>)

$k_3$  = respiration coefficient (day<sup>-1</sup>)

$s_p$  = plankton sedimentation coefficient (day<sup>-1</sup>)

Values for coefficients were used from Mitsch and Reeder (1991). Solar radiation data were obtained from Mitsch (1989), and calculated as a time function after the manner in WASP.

### 4.3 Macrophytic Gross Primary Productivity

The macrophytic productivity equation used, modified after Mitsch and Reeder (1991), is:

$$\frac{dM}{dt} = k_4 IAV - k_5 * C_2 - SDCO * C_2 \quad (3)$$

where:

$C_2$  = macrophyte biomass (kcal m<sup>2</sup>)

$k_4$  = gross primary productivity coefficient for macrophytes, unitless

$k_5$  = macrophyte respiration coefficient (day<sup>-1</sup>)

$SDCO$  = time variable macrophyte sedimentation coefficient (day<sup>-1</sup>)

Values for the coefficients  $k_4$  and  $SDCO$  were after Mitsch and Reeder (1991). The macrophyte respiration coefficient,  $k_5$ , was adjusted from 0.0025 to 0.0030, during calibration.

#### 4.4 Total Phosphorus

The total phosphorus equation is from Mitsch and Reeder (1991), and is as follows:

$$\frac{dP}{dt} = (s_2/d) A - k_1 C_3 - (s_1/d) C_3 - a (k_2 IAV - k_3 C_3) A \quad (4)$$

where:

$C_3$  = total phosphorus (mg/L)

$s_1$  = sedimentation velocity (m day<sup>-1</sup>)

$s_2$  = resuspension velocity (m day<sup>-1</sup>)

$d$  = wetland depth (m)

$a$  = phosphorus/kcal ratio in plankton (mg P kcal<sup>-1</sup>)

$A$  = area of segment (m<sup>2</sup>)

Sedimentation and resuspension velocities were considered site specific to the Old Woman Creek Wetland and therefore the values determined by Mitsch and Reeder (1991) were used. Due to the requirement for steady state volumes in WASP, the wetland depth was held constant during the 275 day simulation period. This is not seen as a serious limitation, as the wetland volume during the particular year data were available, a drought year, was nearly constant after late Spring.

#### 4.5 Copper Uptake by the Macrophyte *Nelumbo lutea*

The copper uptake submodel represents in several respects that heart of the current modeling effort. It is coupled to copper partitioning and speciation, discussed later. Early work to characterize plant nutrient uptake by Nye and Marriot (1969) as reported by Rendig and Taylor (1989) proposed that nutrient uptake rates could be expressed using Michaelis-Menten kinetics, often applied to enzyme-catalyzed reactions. Following the work of Nye and Marriot, Claassen and Barber (1976) proposed a similar model for nutrient uptake. This model, however, requires significant plant-growth data including parameters for initial root length, average root radius, and differential soil buffer capacity for the nutrient.

The Cushman-Barber model (Rendig and Taylor, 1989), is similar to the work of Claassen and Barber, but considers the effects of interroot competition on the rate of nutrient uptake. This model, too, requires plant morphological data beyond the scope of the current modeling effort.

Nielsen (1976 a,b,c) proposed and tested a nutrient uptake model based on Michaelis-Menten kinetics which required data only on the concentration of the substrate (in this case copper) in plants measured at different solution concentration regimes. He found good agreement with modeled and field measurements of copper uptake by barley plants grown in both water and soil cultures. Nielsen's work was conducted in the pH range of 7.1 - 8.3; this is very similar to the pH of the Old Woman Creek Wetland during the 1988 study year.

The basic form of Nielsen's copper kinetics equation as used in this modeling effort is presented below, after Lehninger (1975):

$$\frac{dv}{dt} = \frac{dV}{dt} * \frac{C_a}{C_a + K_M} \quad (5)$$

where:

$v$  = rate of copper uptake, ( $\mu\text{g}$  copper/day  $\text{m}^2$ )

$V$  = maximal rate of copper uptake, ( $\mu\text{g}$  copper/day  $\text{m}^2$ )

$C_a = C_b - C_{MIN}$ , the apparent concentration of copper at the root membrane surface,  $\mu\text{g/L}$

$C_b$  = concentration of copper in bulk solution,  $\mu\text{g/L}$

$C_{MIN}$  = concentration of copper in bulk solution at which  $v = 0$ ,  $\mu\text{g/L}$

$K_M$  = Michaelis-Menten Constant for copper uptake,  $\mu\text{g/L}$ .

The maximal rate of copper uptake,  $V$ , and the Michaelis-Menten constant,  $K_M$ , the concentration of copper in solution at which half of the maximal uptake occurs, are derived knowing only the rate of copper uptake,  $v$ , and the concentration of copper in the bulk solution,  $C_b$ , using either the Lineweaver-Burk double reciprocal or Eadie-Hofstee graphical methods (Lehninger, 1975).

Nielsen (1976 b) used the Lineweaver-Burk method to determine  $V$  and  $K_M$ . Either of these graphical, linear regression methods may induce error in the values of  $V$  and  $K_M$ ; for the current modeling effort, however, the linear regression

technique was assumed to be adequate.

However, data for both the concentration of copper in *Nelumbo lutea* and the concentration of copper in the bulk solution at which this uptake occurred were not available for the present modeling of the Old Woman Creek Wetland (Reeder, 1992). Therefore, system specific values for  $V$  and  $K_M$  could not be determined given available data for the Old Woman Creek Wetland.

Based on Barber's observation that no measurements of copper uptake kinetics other than what Nielsen reported are available in the literature (Barber, 1984), and because research for the work reported here revealed no additional measurements, Nielsen's values for  $V$  and  $K_M$  were used for the current modeling effort. The use of Nielsen's constants is further supported by the similarity in pH between his work and the pH of the Old Woman Creek Wetland, discussed earlier.

It is recognized, however, that this approach represents a limitation; the determination of  $V$  and  $K_M$  under conditions present at the Old Woman Creek Wetland, using the macrophyte *Nelumbo lutea* represents a clear research need requiring on-site field work.

The determination of an accurate value for  $C_{MIN}$ , the concentration of copper in solution at which no uptake occurs, was equally troublesome. Although Nielsen (1976b) calculated a mean  $C_{MIN}$  value of  $0.045 \pm .008 \mu\text{mol Cu-ions}$ , research by Boyd (1978) and Barber (1984) has shown that background concentrations of copper in aquatic macrophytes and copper toxicity is both species and community specific.



Barber (1984) noted that free copper ( $\text{Cu}^{2+}$ ) in solution reported in the literature at that time ranged from 0.0001 to 0.005  $\mu\text{mol/L}$ , much lower than the value reported by Nielsen. Barber argued that plants are apparently able to "obtain sufficient copper under these conditions"--suggesting that Nielsen's value for  $C_{\text{MIN}}$  is too high. However, Barber noted that the information on copper uptake did not include a discussion of the pH at which uptake occurred. Sylva (1976) noted that very little free copper is expected in the pH range of 6.5 - 8.0, and that the presence of complexing agents can further reduce the amount of free copper in solution.

The Old Woman Creek Wetland, with high suspended solids concentrations and a pH between about 7.0 - 8.5 in both water column and sediments, would also appear to have little free copper in solution. Therefore, since Nielsen's work was conducted in a pH range similar to the Old Woman Creek Wetland, the assumption was made the Nielsen's value for  $C_{\text{MIN}}$  was satisfactory for the current modeling effort.

Research has shown that, in general, the greatest copper uptake potential occurs in rooted, emergent macrophytes (Boyd, 1970, 1978). These plants differ from floating leafed macrophytes (such as the water hyacinth, and the waterlily *Nelumbo lutea* modeled here) and submerged and partially submerged macrophytes (Cooley *et al.*, 1979) in that they derive the majority of their nutrients from sediments. Thus, rooted emergent macrophytes appear to offer the greatest potential for nutrient removal in wetland eco-systems where, typically, sediments are the predominant sink for nutrient loads. However, as the available data were for the floating leafed macrophyte *Nelumbo lutea*, the current modeling effort focused only on the uptake

of copper from the dissolved copper pool in the water column.

#### **4.6 Litter Decomposition and Nutrient Cycling**

Litter decomposition is an important dimension in the cycling of nutrients in wetland ecosystems (Likens, 1974; Klopatek, 1974; Odum and Heywood, 1978; and Davis and van der Valk, 1978 a, b); the effects of litter on the dissolved copper pool were considered as a sub-system to the copper uptake system. A set of six simple algebraic equations as described by Davis and van der Valk (1978 a) were used to characterize the amount, rate of decomposition, and eventual addition of copper to the water column as a function of litter kinetics. Sloughing and decomposition of litter was modified after work by Hydrosience (1975), which describes these processes in terms of both seasonality and temperature.

Live biomass acts as a temporary storage medium for nutrients; the potential to remove nutrients from the wetland system exists if this nutrient-laden biomass is harvested. This technique, which can effectively extend the life of a system to remove nutrients, is discussed later.

#### **4.7 Copper Partitioning and Speciation**

The amount and type of copper in a wetland is affected by adsorption-desorption, organic and inorganic complexation, and precipitation reactions. The partitioning of

copper between dissolved, colloidal, and particulate fractions occurs in aquatic environments, and is largely driven by the concentration of suspended solids (Thomann and Mueller, 1987). According to Sylva (1976), the most significant removal mechanism for copper is through the precipitation of *malachite*,  $\text{Cu}_2(\text{OH})_2\text{CO}_3$ . For the present work, copper was considered to exist in either a dissolved or particulate phase, the latter phase including colloidal forms of copper.

Partitioning of copper between dissolved and particulate phases was modeled after Thomann and Mueller (1987). The partitioning coefficient,  $\eta$ , is the ratio of copper at equilibrium between the particulate and dissolved form. Because the kinetics of sorption-desorption are considered "fast", continuous equilibration between the two phases is a valid assumption (Thomann and Mueller, 1987).

The partitioning coefficient is defined as:

$$\eta = r/c_d \quad (6)$$

where:

$r$  = solid phase concentration of the species expressed as  $\mu\text{g}$  per kg dry weight of solids

$c_d$  = aqueous phase concentration of the species expressed as  $\mu\text{g}$  per bulk volume (volume of water + volume of suspended solids), in liters

The particulate phase of copper,  $c_p$ , is represented as the amount of solid phase bound to suspended solids in either the water column or sediments. The equation is simply:

$$c_p = \eta m \quad (7)$$

where:

$m$  = suspended solids concentration, in either the water column or sediments

Alternatively:

$$c_p = \Psi m c_d \quad (8)$$

Given equations 6-8, and that the total concentration of copper in the system,  $c_t$ , is given by:

$$c_t = c_d + c_p \quad (9)$$

then the total concentration of copper can also be given by:

$$c_t = (1 + \Psi m) c_d \quad (10)$$

The fraction of copper which is in the dissolved form,  $f_d$ , can then be expressed as:

$$f_d = c_d / c_t \quad (11)$$

or

$$f_d = (1 + \Psi m)^{-1} \quad (12)$$

Particulate copper as a fraction of total copper can be given by:

$$f_p = 1 - f_d \quad (13)$$

then:

$$c_p = f_p c_t \quad (14)$$

and

$$f_p = \Psi m / 1 + \Psi m \quad (15)$$

The partitioning coefficient for copper in the water column was set at 43,000 L/kg, and 6,000 L/kg for the sediments, indicating a greater fraction of dissolved versus particulate copper in the water column, and a greater fraction of particulate versus dissolved copper in the sediments (Thomann and Mueller, 1987).

In addition to partitioning, the amount of copper in either phase was also a function of the sedimentation rate of suspended solids, which was quite slow due to the shallow depth of the system (average depth = .41 m), relative to the high rate of resuspension (Mitsch and Reeder, 1991). Dissolved copper removed from the water column by macrophytic uptake was considered as a sink (loss) of copper, which was temporarily stored in the macrophyte biomass until sloughing and decomposition of litter returned copper back to the water column as a source (gain).

The speciation of copper, once the model calculated the fraction of the metal in both the dissolved and particulate phases, was performed by MINTEQA2 (Allison *et al.*, 1990). MINTEQA2 allows the calculation of metals speciation in environmental settings; it is considered to be a "state of the art" example of equilibrium solution chemistry software currently available. After work by Badruzzaman and Lung (1991), the model was developed so that at each time step and segment in the model, MINTEQA2 is called and speciation of copper is calculated.

Since macrophytes were considered in this model to adsorb only dissolved copper, the speciation of copper by MINTEQA2 represents a significant link in the accurate calculation of copper uptake in macrophytes. Furthermore, as research indicates

that metal speciation, and the interactions among several metals affects the rate of sedimentation, biouptake, and plant toxicity (Chen, 1985; Jamil *et al.*, 1986), the use of MINTEQA2 in the current setting is invaluable.

Sylva (1976) showed that speciation of copper is predominantly a function of pH. In the pH range of 6.5-8 (defined by Sylva as the pH of "greatest interest" in a natural water), copper speciation occurs most rapidly. For example, at a pH < 5, copper exists almost entirely as copper (II), or  $\text{Cu}^{2+}$ . At a pH of 7, however, a variety of forms of copper may exist, such as  $(\text{CuOH})^{1-}$ , and  $\text{CuCO}_3$ , among others. Given the pH conditions in the wetland, little  $\text{Cu}^{2+}$  was expected to occur, and  $\text{Cu}^{2+}$  toxicity was not expected to be an issue.

The Old Woman Creek Wetland appears to be well buffered, with pH of both water column and sediments exceeding 7 during nearly all of the study period (Mitsch, 1989). Thus, great propensity existed during the study period for speciation of copper to occur.

#### 4.8 Suspended Solids

The concentration of suspended solids was calculated as a function of rates of sedimentation, settling loss, and bioturbation of sediments. An initial settling velocity was chosen after Mitsch and Reeder (1991) at .0984 ft/day. This rate was later calibrated to a settling rate of .0125 feet/day in order to better predict the average suspended solids concentration in the Old Woman Creek Wetland during the

1988 study period. Sedimentation and resuspension velocities were after Mitsch and Reeder (1991). The effects of plankton respiration were included in the calculation of suspended solids, although the concentration of suspended solids did not vary considerably when plankton effects were excluded.

## 5. RESULTS OF ANALYSIS

Calibration of the model was planned using data from several sources on the Old Woman Creek Wetland, in northern Ohio. Early calibration efforts were completely unsuccessful. Accurate calibration did not occur until the wetland depth, reported in several places in the literature at a mean depth of about 4.1 meters during the study year (1988), was found to be off by an order of magnitude and corrected to .41 meters.

The change in depth necessitated modification of the initial model from a two-layer, stratified system, to a completely mixed one water layer system. In the end, this simplified the model; however, it is easily modified to reflect deeper, two-layer systems. Following these changes, calibration occurred very rapidly.

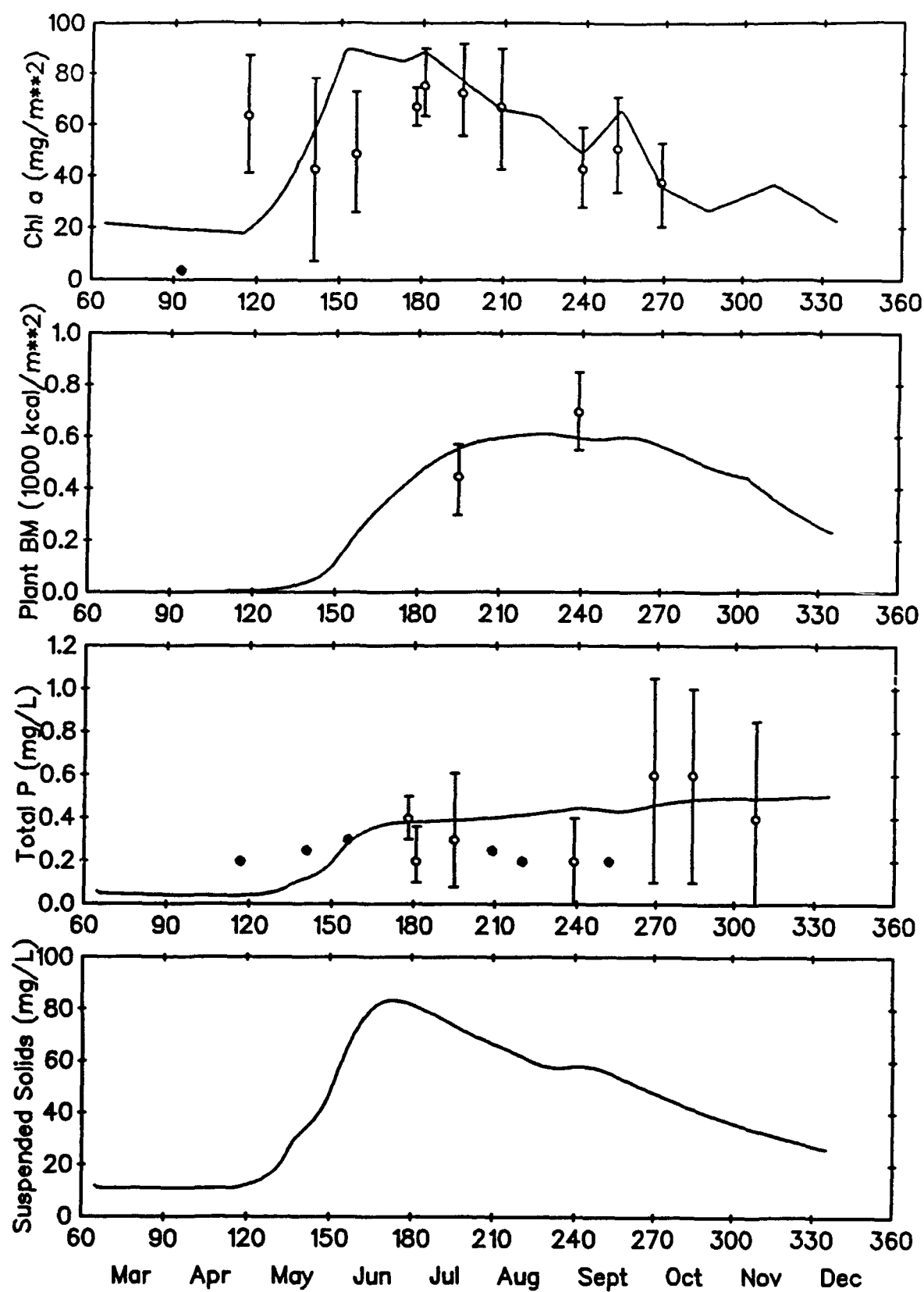
Only minor adjustments to the values of coefficients reported by Mitsch and Reeder (1991) in their modeling effort were made: the only significant change was to the value for  $k_s$  (unitless), the macrophyte gross primary production coefficient, which was changed from 0.0025 to 0.0030. This approach represents both a validation of Mitsch and Reeder's work and the current modeling effort, especially in view of the software used by Mitsch and Reeder (STELLA<sup>TM</sup>) and that used for the current modeling effort, WASP.



### 5.1 Sub-Model Calibration (Old Woman Creek Wetland)

The results of model calibration appear in Figure 5.1. Modeled results for chlorophyll-*a* ( $\text{mg}/\text{m}^2$ ), biomass of the dominant macrophyte *Nelumbo lutea* ( $\text{kcal}/\text{m}^2$ ), and total phosphorus ( $\text{mg}/\text{L}$ ) agree well with the data. Range bars on data indicate one standard deviation (Mitsch and Reeder, 1991). A separate plot of chlorophyll-*a* expressed as  $\text{kcal}/\text{m}^2$  day (not shown) also agreed well with the data. These results agree fairly well with the pattern reported by Thomann and Mueller (1987), who note that the concentration of phytoplankton peaks in late Spring, and again during early Fall due to the effects of nutrient recycling.

Macrophyte biomass production became significant only after about time = 110 days. Data for macrophyte biomass is presented after the quadrant method of harvesting (Mitsch, 1989). The data for macrophytes corresponds to  $101 \pm 32$  gr d.w. biomass/ $\text{m}^2$  (July 12, 1988), and  $160 \pm 30$  gr d.w. biomass/ $\text{m}^2$  (August 25, 1988). The conversion from grams biomass to kcal biomass is approximately 4.45 kcal/gram. According to Mitsch and Reeder (1989), typical aquatic macrophyte productivity is about 500 gram (d.w.)/ $\text{m}^2$ , or about 4-5 times as productive as *Nelumbo lutea* reported here. The implications this has on the uptake of copper from the system are discussed later.



**Figure 5.1: Calibration of the Model Using Chlorophyll-*a*, Macrophyte Biomass, and Total Phosphorus, and Calculation of Suspended Solids**

Calibration for total phosphorus in the water column was achieved within consistent limits, despite the constant wetland volume and depth limitations imposed by WASP. While the results are consistent with available data, the model did not predict a higher concentration of total phosphorus during the high runoff period in early Spring.

Previous modeling of total phosphorus in the Old Woman Creek Wetland predicted phosphorus concentrations of about 2.40 mg P/L for early Spring (Mitsch and Reeder, 1991). At first the discrepancy was thought to be attributed to the data source for phosphorus loading. Mitsch and Reeder used an average phosphorus loading from Baker (1988); phosphorus data for the current modeling effort were from Mitsch and Reeder (1989 b).

The model was run using both sets of data; however, no significant differences in phosphorus concentration over the 275-day modeling period were noted between data sets. Since there are no data on total phosphorus concentrations in the water column during early Spring, however, it is difficult to conclude that the current results are in error during the Spring runoff period. Given the acceptable fit of the results for the periods for which data were available, it is reasonable to accept the modeled calculations.

## **5.2 Suspended Solids**

Model results for suspended solids are shown in the bottom frame in Figure 5.1,

at the calibrated suspended solids settling velocity of .0125 ft/day. Data for suspended solids in inflow was from Mitsch and Reeder (1989 b).

The suspended solids settling velocity used in the initial modeling was .0984 ft/day (Mitsch and Reeder, 1991). While the model calculation of suspended solids at this velocity is within one standard deviation of the average wetland value (Mitsch and Reeder, 1989 b), the model generally under predicted total suspended solids. This may be due to the WASP steady state limitation, lack of inflow after about day 190, or failure to capture a resuspension mechanism within the wetland which maintains the suspended solids at a higher concentration in the water column. The settling velocity was revised to .0125 feet/day, which raised the total suspended solids concentration to a peak of about 90 mg/L. While this is still below the peak reported by Mitsch and Reeder (1989 b), further adjustment of the settling velocity without physical basis was deemed inappropriate.

### **5.3 Copper Predictions in the Water Column and Sediments**

After the model was calibrated against chlorophyll-*a*, macrophyte biomass, and total phosphorus, the next step was to evaluate the results of dissolved and particulate copper modeling, which were tied to copper uptake by macrophytes and litter kinetics. Although there were no data available on the exact concentration of copper in the water column or sediments during the 1988 study period, average values for copper in the water column and sediments were available in Frizado *et al.*

(1986). Minimum and average copper concentrations reported in inflow to the Old Woman Creek Wetland ranging from 0.001 mg/L to 0.0305 mg/L, respectively, were modeled. These values are cited as typical copper concentrations (Frizado *et al.* 1986) of waters draining into the Old Woman Creek Wetland. Initial values for particulate copper in the water column, and dissolved copper in the sediments, were calculated from the copper partitioning coefficient discussed earlier.

The kinetics of dissolved copper concentrations in the water column include sink and source terms related to macrophyte kinetics, as discussed. Figures 5.2 - 5.3 depict the concentration of dissolved copper at the two copper inflow concentration regimes.

At the minimum concentration, the concentration of dissolved copper is below the level at which uptake by macrophytes occurs; macrophyte uptake does not occur until about day 155 (Figure 5.9, upper frame), and the copper concentration in the water column is therefore unaffected by macrophyte growth or litter kinetics.

As the macrophytic biomass increases, copper is removed from the water column, but this is offset during the initial growth of the macrophyte by the return of copper to the water column by litter sloughing and decomposition. After about day 210, macrophyte growth reaches a peak and levels off until about day 250, and the dissolved copper pool in the system is decreased due to the dominant copper removal mechanism of macrophytic copper uptake. An increase in the dissolved copper pool is seen after day 288, when the sloughing fraction of litter increased from 0.01 to 0.018 (unitless) after Hydrosience (1975).

At an average copper inflow concentration of 0.0305 mg/L, macrophytic copper uptake occurred at the start of the growing season, about day 110. A sharp dip in the dissolved copper pool was noted at this time, signalling the beginning of the macrophytic copper uptake "pump".

At this higher concentration of copper in the inflow, more copper was available to the macrophyte for uptake, and macrophytic uptake had a marked effect on the dissolved copper pool beginning about day 160, and continuing until day 270, when the dissolved copper concentration began to rise. This appears to be consistent with the work of several authors reported earlier: copper uptake is dependent on the amount of copper available in the system.

A sharper increase in copper added from the sloughing and decomposition of litter was also apparent. At both concentrations of copper in the inflow, low concentrations of dissolved copper were evident at the time of peak biomass, about day 240. Figures 5.2 and 5.3 reveal, therefore, the function of the macrophyte in reducing the dissolved copper pool in the water column. After day 288, the amount of dissolved copper increased significantly, as the rate of copper addition due to litter nearly doubled. This corresponds to an increase in the amount of copper-laden litter sloughed-off into the water column. Thus, the kinetics of macrophyte growth, copper uptake, and litter decomposition kinetics appear to be correctly linked in the model.

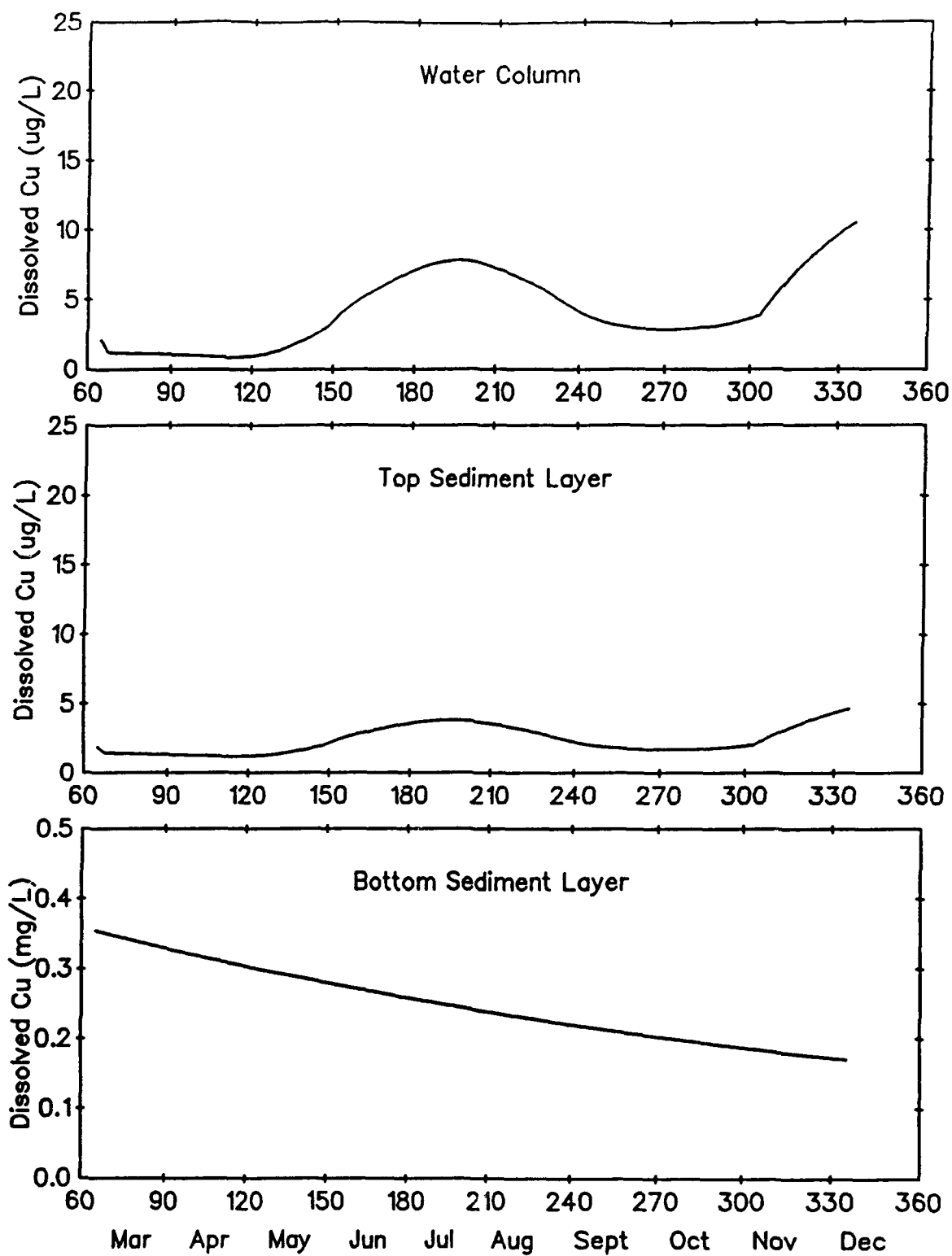


Figure 5.2: Total Dissolved Copper at .001 mg/L Copper Concentration in Inflow

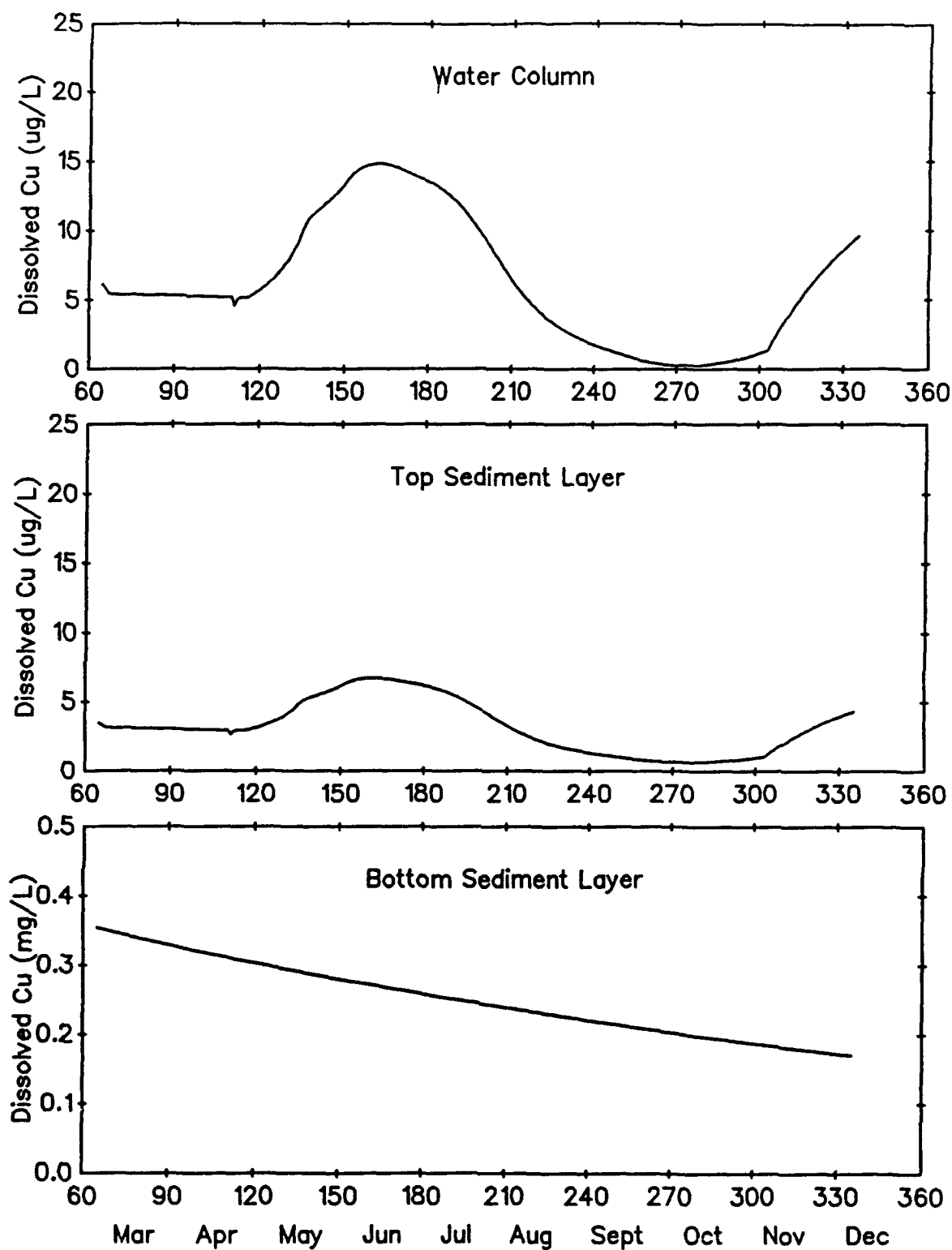


Figure 5.3: Total Dissolved Copper at .0305 mg/L Copper Concentration in Inflow



Dissolved copper in the sediment layers (in units of volume of porewater) follows predictable patterns. In the top sediment layer, diffusion of dissolved copper against a concentration gradient is reflected in similar concentration curves for the top sediment layer and copper in the water column. In this regard, *Nelumbo lutea* appears to be effectively pumping dissolved copper from the top sediment layers, even though copper uptake by this macrophyte is modeled to occur from the water column.

This interesting phenomenon challenges the notion that floating macrophytes cannot affect the level of copper in wetland sediments. However, macrophytic copper uptake does not, as expected, affect dissolved copper concentrations in the deeper bottom sediment layer, which is more isolated than the top sediment layer. This is demonstrated by the nearly constant concentration of dissolved copper in the bottom sediment layer.

The concentrations of particulate copper also appear to be modeled accurately, as shown in Figures 5.4 - 5.5. As the top sediment layer represents a transition zone between the water column and deeper sediments, particulate copper is only slightly higher than that in the water column. A relatively "slow" sedimentation rate of .74 cm/year (Reeder, 1989) was used to model the loss of a solid particle from the bottom sediment layer to yet deeper sediments. While the concentration of particulate copper in the bottom sediment was expected to be more constant, further adjustment of this sedimentation rate was not done. The physical basis for the loss of copper from deep sediments is unknown at this time. However, the loss of

particulate copper may be a function of an incorrect partitioning coefficient for the sediments; the use of 1986 copper data for the 1988 study period; or numerical dispersion induced by the calculation of an average copper concentration in the 50 centimeter-deep bottom sediments using the 1986 data.

Figures 5.6-5.8 illustrate the role of suspended solids on the concentration of particulate copper in the water column. Figure 5.6 represents the concentration of suspended solids at a "fast" settling velocity of .0984 ft/day (the value initially chosen for calibration). Figures 5.7 and 5.8 demonstrate the effect of reduced suspended solids in the water column on the particulate copper concentration, at copper inflow concentrations of .001 mg/L and .0305 mg/L, respectively.

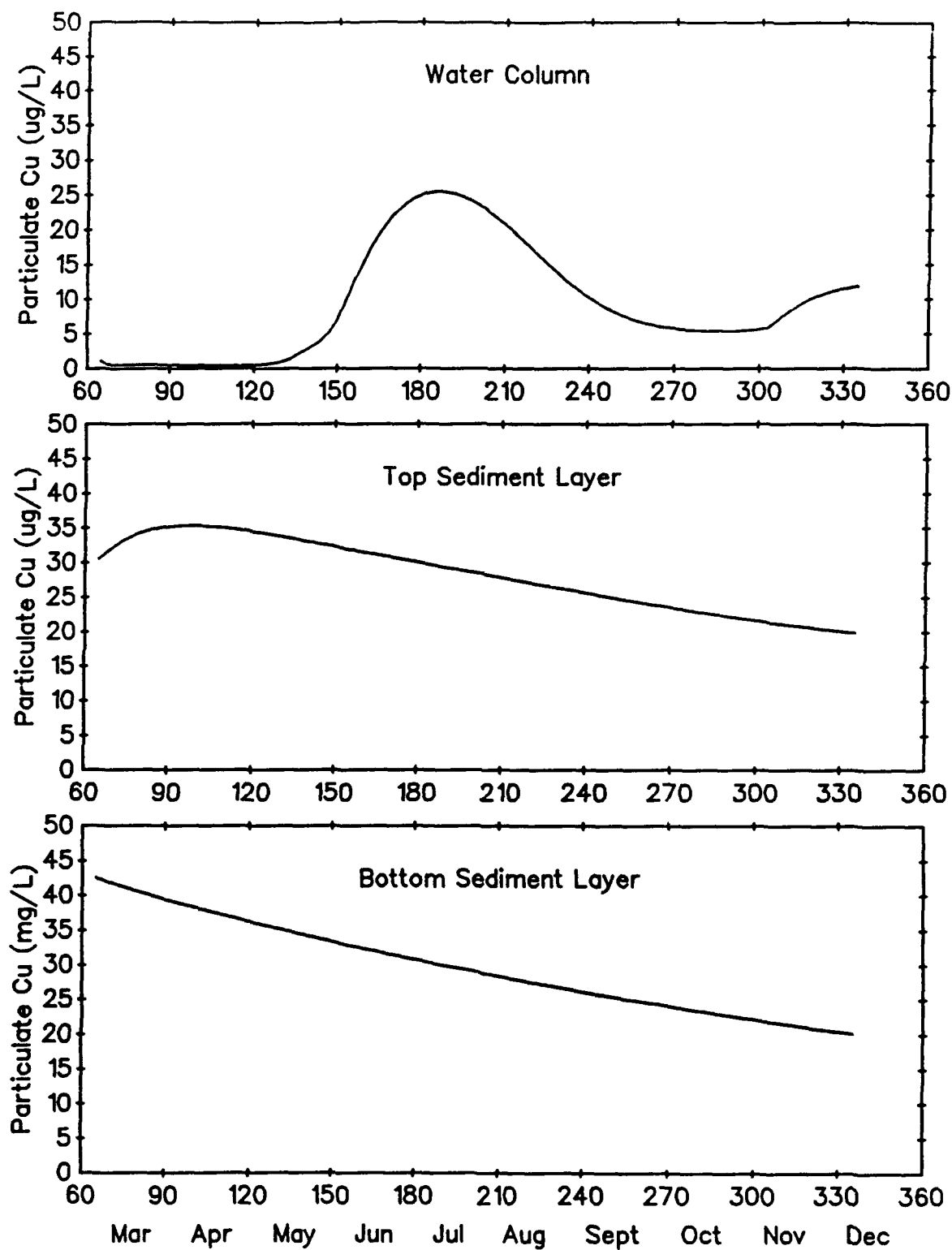


Figure 5.4: Particulate Copper at an Inflow Copper Concentration of .001 mg/L

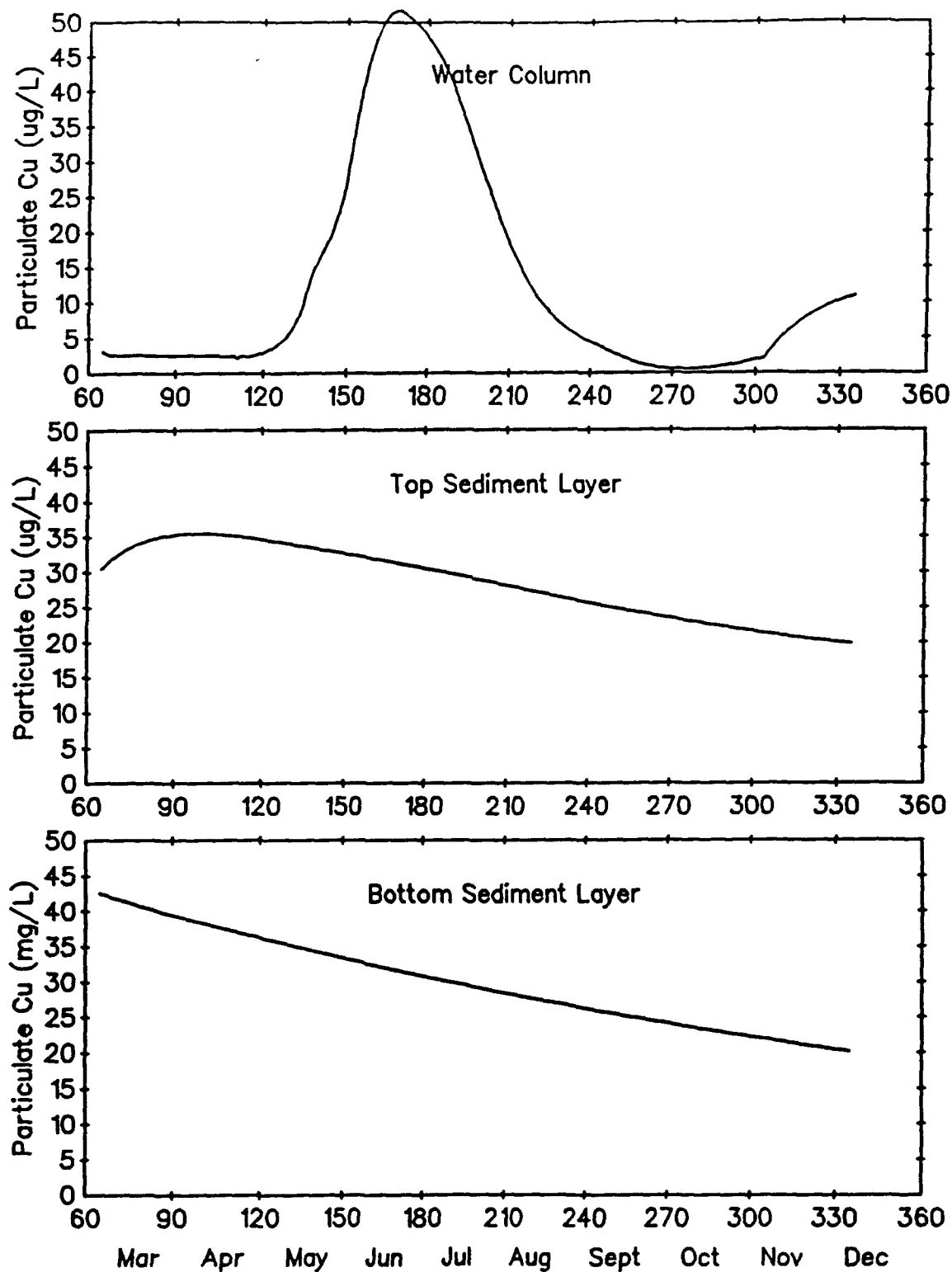
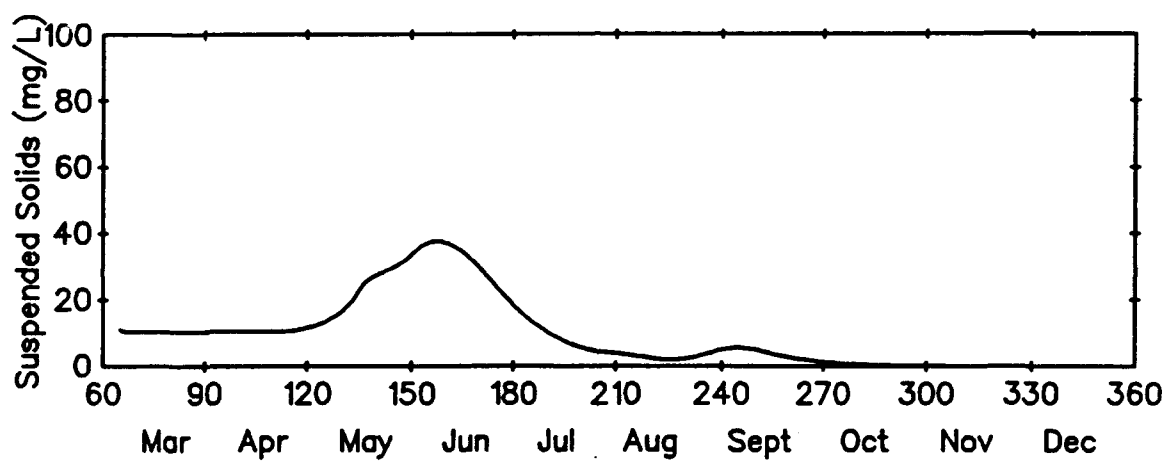
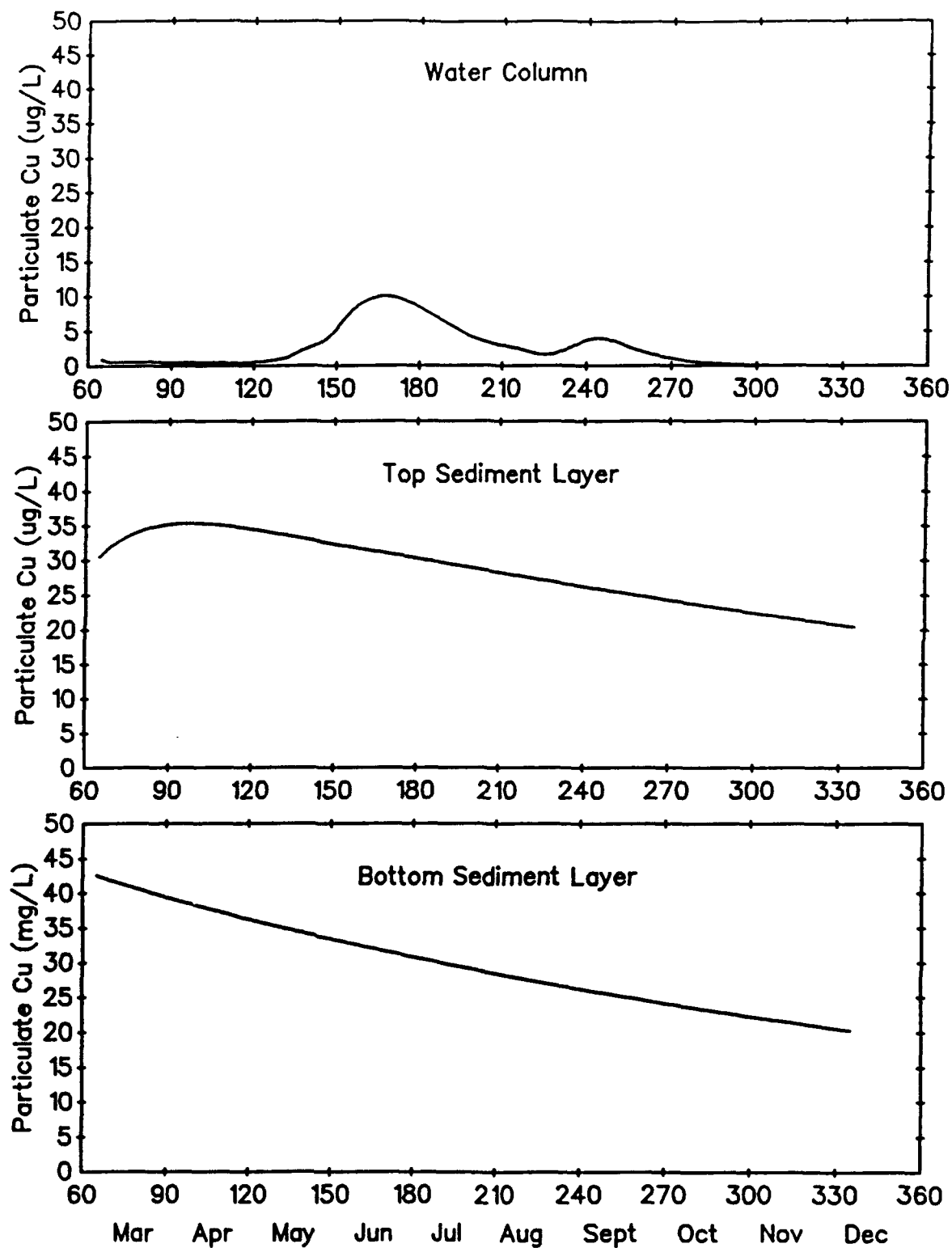


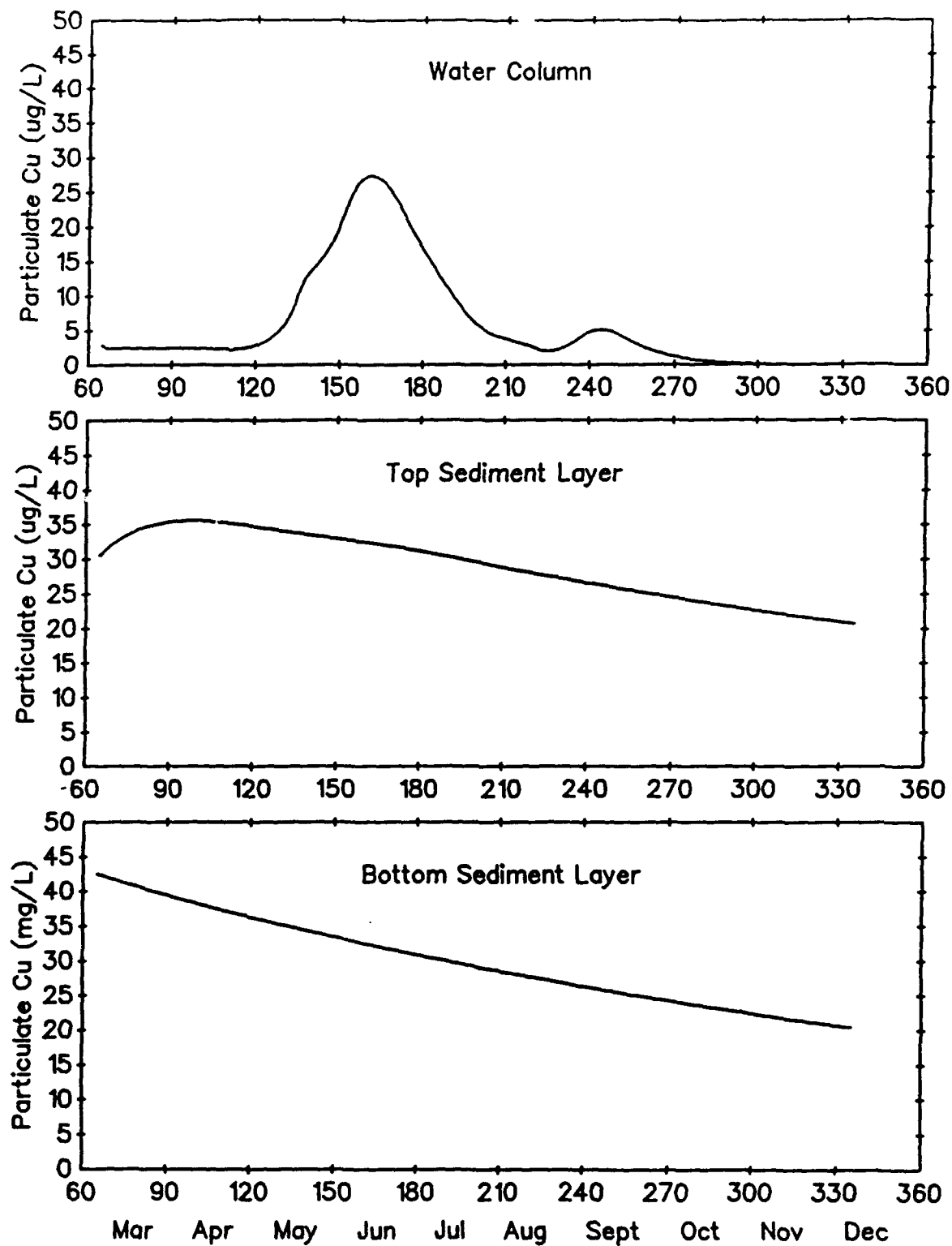
Figure 5.5: Particulate Copper at an Inflow Copper Concentration of .0305 mg/L



**Figure 5.6: Suspended Solids Concentration at Settling Velocity of .0984 ft/day**



**Figure 5.7: Particulate Copper Concentration at a Settling Velocity of .0984 ft/day at Copper Inflow Concentration of .001 mg/L**



**Figure 5.8: Particulate Copper Concentration at Settling Velocity of .0984 ft/day at Copper Inflow Concentration of .0305 mg/L**

#### 5.4 Copper Predictions in the Biomass of *Nelumbo lutea*

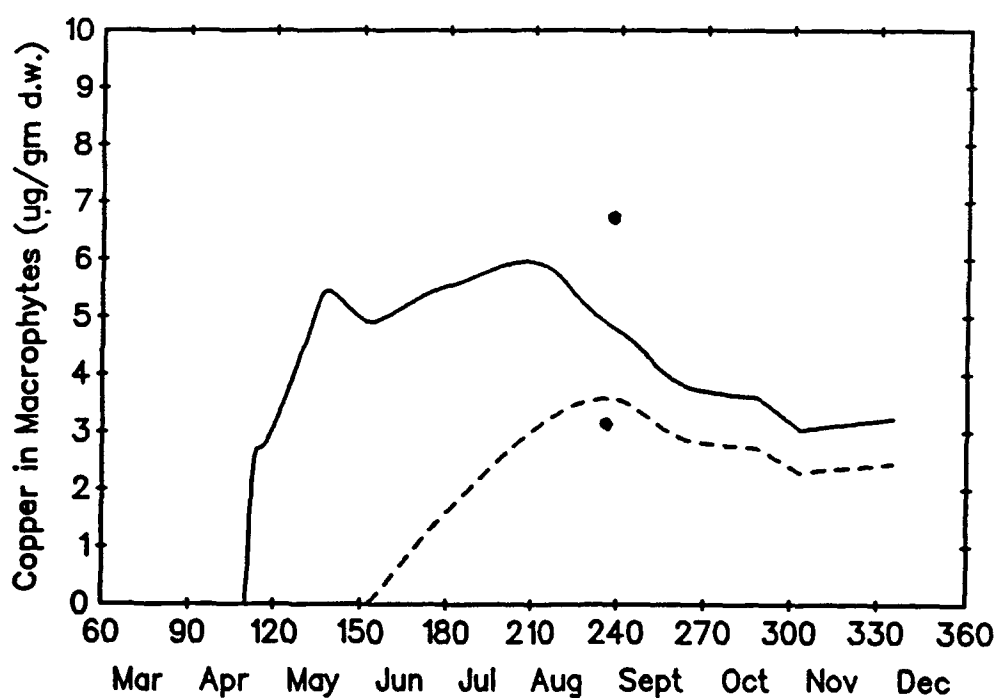
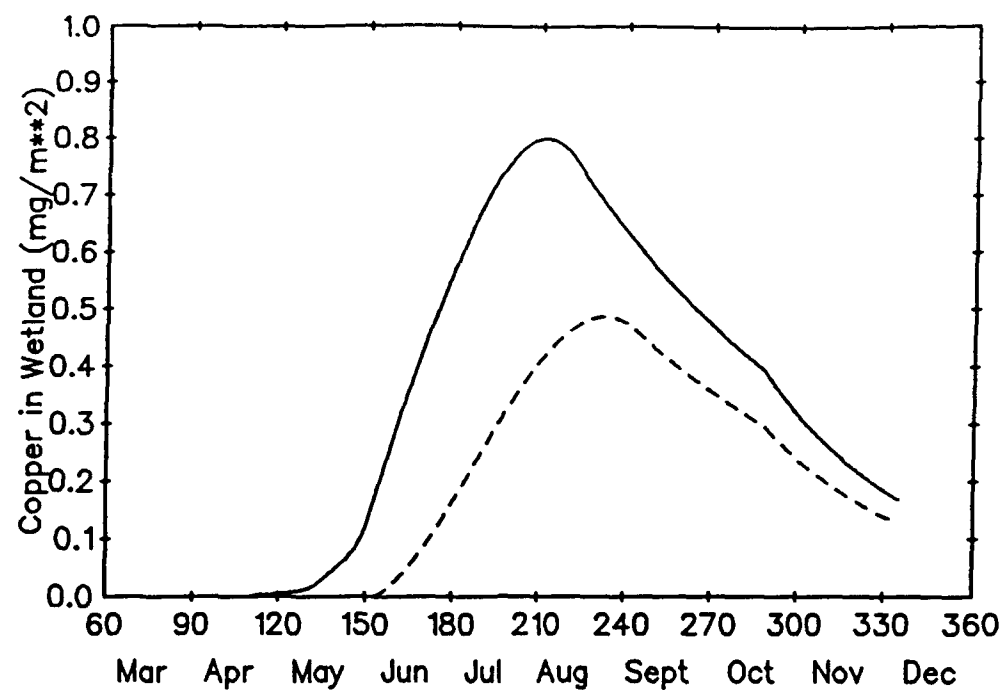
Figure 5.9 depicts the concentration of copper in  $\mu\text{g}$  per gram dry weight of biomass during the growing season (about day 110 to the first frost, day 303), at the two concentrations of copper in inflow to the wetland discussed previously. Limited data (Reeder, *personal communication*, unpublished data, 1992) are indicated at peak biomass, about day 240, and show a close agreement between the modeled copper uptake of *Nelumbo lutea* using the Michaelis-Menten equation as modified after Nielsen (1976 a,b,c). The data from Reeder consisted of measurements of copper ( $\mu\text{g}$  copper/gram dry weight biomass) in 15 *Nelumbo* plants harvested at peak biomass during the study period (mean =  $6.77 \pm 1.6 \mu\text{g}$  copper/gr d.w.). If data for the concentration on harvested flower heads are included ( $n = 2$ , @ 18.17 and 17.39  $\mu\text{g}$  copper/gr d.w.), then the mean concentration is  $8.06 \pm 3.94 \mu\text{g}$  copper/gr d.w. biomass.

At the low concentration of copper modeled in the inflow to the wetland, the peak copper concentration occurred almost exactly on day 240. At the higher concentration of copper in the inflow, the peak copper concentration occurred earlier, at about day 215, reflecting the increase in the dissolved copper pool at the higher copper concentration in the inflow. Considering the complexity of the wetland ecosystem, and the lack of complete site-specific data with which to derive the Michaelis-Menten constants  $V$  and  $K_M$ , the modeled results appear to be acceptable.



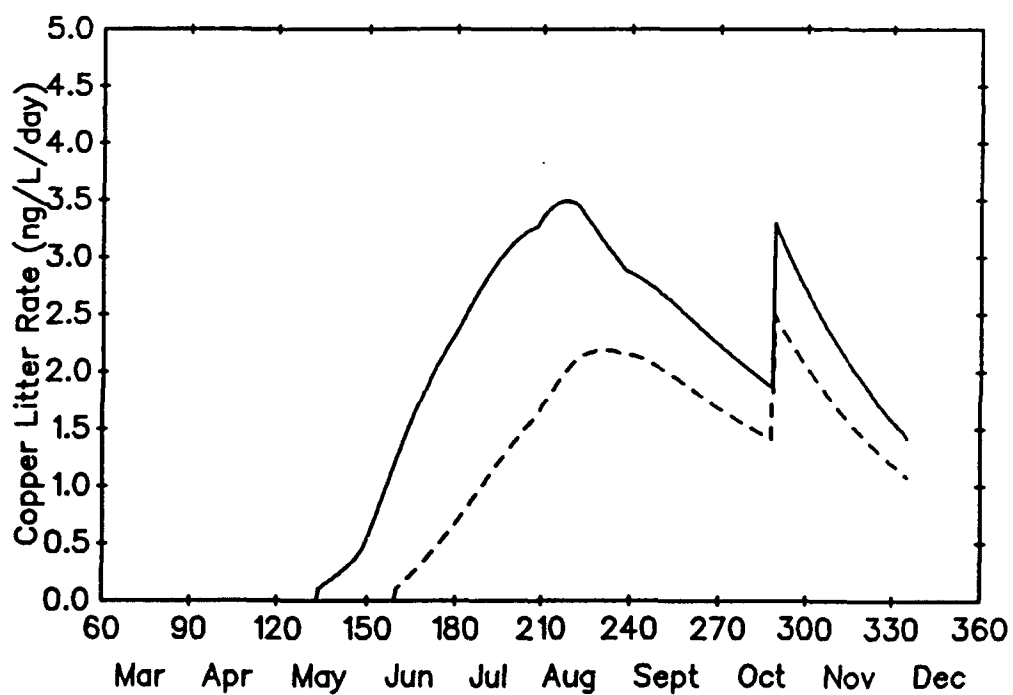
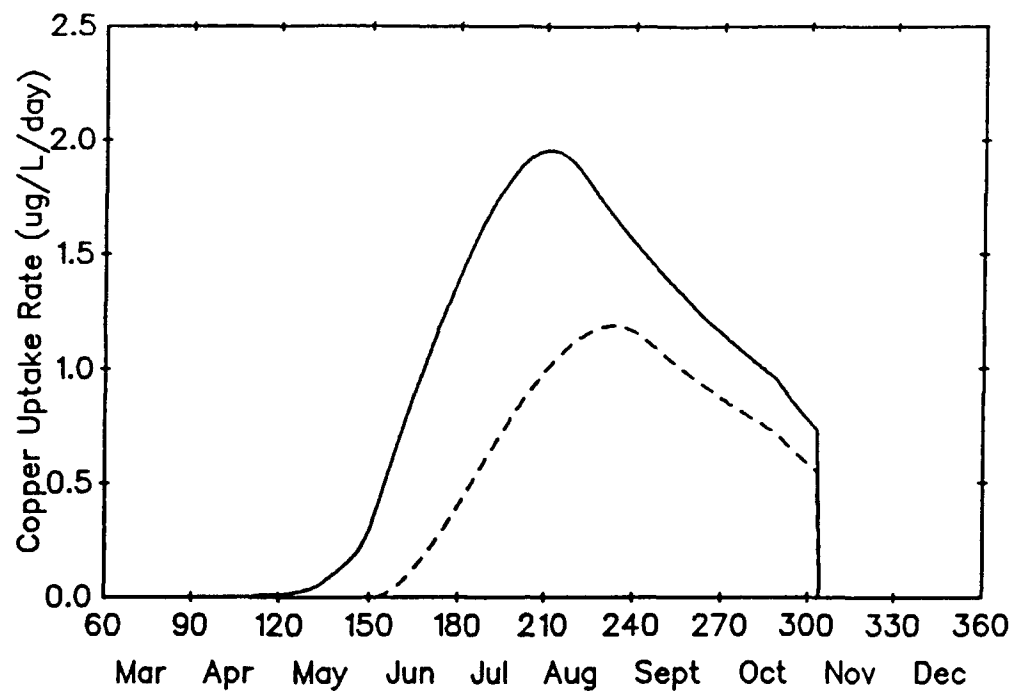
The top frame of Figure 5.10 depicts the rate of copper removal from the dissolved copper pool in the water column as a function of macrophyte copper uptake, in  $\mu\text{g/L day}$ , at two copper concentrations. It is clear that the availability of copper has a significant effect on the level at which macrophytes act as a copper "pump" to remove dissolved copper from the water column. Note that after the first frost, about day 303, uptake goes to zero.

Given the relative concentrations of copper in both the water column and sediments, the latter appear to be the primary removal pathway for copper in the Old Woman Creek Wetland, and this is consistent with research by others. However, the results presented here clearly show that macrophytic plants have a role in copper removal. Recalling that the beds of *Nelumbo lutea* reported here are only about one-fifth as productive as typical macrophyte stands (Mitsch and Reeder, 1991), it is reasonable to predict that in more productive systems macrophytes can function as the dominant copper removal mechanism. It is interesting to note that the concentration of copper in *Nelumbo lutea* reported here is about one-fifth of the typical concentration cited by Cowgill (1974) and Boyd (1978) of about  $40 \mu\text{g/gr d.w.}$



Legend: — Avg. Copper Loading Rate  
--- Low Copper Loading Rate

Figure 5.9: Copper Uptake Rate and Copper in *Nelumbo lutea*



Legend:      — Avg. Copper Loading Rate  
              --- Low Copper Loading Rate

**Figure 5.10: Copper Removal and Addition Rates at Two Copper Concentrations**

### 5.5 Copper Speciation Performed by MINTEQA2

Analysis of MINTEQA2 copper speciation results revealed that the primary form of dissolved copper in the water column (>99%) was  $\text{Cu}(\text{OH})_2$ . Free copper, as  $\text{Cu}^{2+}$ , was not represented in any of the three model segments, as expected given the relatively high pH conditions. None of the copper was shown by MINTEQA2 to have precipitated.

In the top sediment layer, copper was represented in the aqueous phase as  $\text{CuCO}_3$ , and as the charged species  $\text{Cu}(\text{CO}_3)_2^{2-}$  (usually about 66%), and  $\text{CuOH}^+$ . In the bottom sediment, the same phases and species of copper were calculated by MINTEQA2, except that  $\text{CuCO}_3$  aqueous held a slightly greater share of the total copper. Insofar as copper was believed to be favored in the sediments in the particulate phase, this may explain the greater than expected loss of particulate copper in the sediments.

It is also interesting to note that despite the presence of sulfate in the wetland, no generation of hydrogen sulfide,  $\text{H}_2\text{S}$ , was noted in either the water column or sediment layers. For the water column, this is consistent with the shallow depth of the wetland, and probable high rates of wind reaeration. While the lack of  $\text{H}_2\text{S}$  in the sediments does not necessarily indicate that the sediments are aerobic, the results do indicate, at least, that sulfate is not being reduced.

## 5.6 Effect of Litter Cycling and Harvested Biomass

As biomass harvesting of vegetative wetlands growth is explored and expanded (e.g., to produce food, fertilizer or fuel), information relative to the heavy metal content of wetland biomass becomes important as well, and has been identified as a research need (Davidson, 1986). The harvest of vegetation at peak biomass can remove relatively large amounts of copper, and allow the wetland to continue to receive copper-laden effluents without reaching a concentration of copper which may be toxic to wetland fauna and flora. For example Blake *et al.*, (1986), has shown that harvesting allows the removal from the system of 25-42% of zinc in *Typha latifolia*.

The bottom frame of Figure 5.10 depicts the rate of copper addition by *Nelumbo lutea* in  $\mu\text{g copper/L day}$ , and allows the calculation of potential copper removal by harvesting biomass. Given the relatively small fraction of the plant biomass which was considered to have "sloughed off" during the study period (.01 from day 61 through 288; .018 after day 288), and the slow rates of litter decomposition which effect the rate of copper return to the water column, the litter kinetics appear to be described accurately.

Furthermore, although the current modeling effort did not extend past day 335 (the period for which data were available), litter sloughing and decomposition will continue to return copper to the wetland until all biomass is gone. Thus, although the rate of copper addition by litter appears small, all copper adsorbed by the

macrophyte biomass should eventually be returned to the wetland. Harvest of the copper-laden biomass represents a method to "short-circuit" this process, and is discussed below.

Given the results presented here for the Old Woman Creek Wetland, and assuming a total wetland area of 56 ha, one-third of which is considered to be covered by biomass, then copper removal potential is easily calculated at any level of copper per m<sup>2</sup>. At a macrophyte copper concentration of 400.0 µg/m<sup>2</sup>, for example, biomass harvesting could remove some 70.0 grams of copper.

If the total wetland were covered with biomass, some 224.0 grams could be removed. While these numbers are small, they may represent the total loading of copper under typical scenarios (e.g., effluent polishing from a municipal POTW). Furthermore, greater potential exists using biomass harvest for copper removal in productive wetland ecosystems, where typical biomass production is often five times as high as the productivity report here for *Nelumbo lutea* in the Old Woman Creek Wetland (Mitsch, 1989). Thus, as the potential for copper removal by biomass harvesting appears small in the natural Old Woman Creek Wetland, in more productive systems it appears to represent an effective method to increase the longevity of the wetland system to remove metals.

## 6. SUMMARY AND CONCLUSIONS

### 6.1 Summary

A computer model has been developed which evaluates microphytic and macrophytic biomass and productivity; total phosphorus in the water column; copper uptake by the macrophytic plant *Nelumbo lutea*; litter sloughing and decomposition; copper partitioning and speciation; and suspended solids in a freshwater wetland in northern Ohio. The model considered the key chemical, physical, and biological processes necessary to predict the interactions among these variables. The Water Quality Analysis Simulation Program (WASP) is the primary software which drives the model and calculates hydrodynamic mass transport; a kinetics subroutine package, WASPB, served as the framework for submodel development. Metals speciation was achieved using the E.P.A. metals speciation model MINTEQA2 at every time step and in every segment to predict the behavior of copper in this well-buffered wetland eco-system.

Calibration of the model was accomplished using data from the study area for 1988 and earlier; the model accurately predicts the concentrations and productivity rates for chlorophyll-*a* and the macrophyte *Nelumbo lutea*, and the concentration of total phosphorus in the water column. Michaelis-Menten kinetics proposed by Nielsen were applied to the calculation of the copper concentration in the dominant macrophyte species *Nelumbo lutea*, a floating leafed plant which was considered to

adsorb copper through its roots in contact with dissolved copper in the water column. Available data indicated that the model accurately predicts the concentration of copper in this macrophyte. Finally, the effects of copper-laden litter sloughing and decomposition on the copper cycling in the wetland were evaluated. Biomass harvesting to remove copper from the wetland system was assessed, and while the potential copper removal in the studied wetland was relatively small, biomass harvesting holds potential for greater copper removal at high copper loading rates in highly productive ecosystems.

## **6.2 Conclusions**

Like most modeling of natural ecosystems, wetland modeling is a formidable task: the goal of accurately characterizing all of the key parameters and processes in natural systems immediately becomes a trade-off between completeness and the availability of data and time. Insofar as this work represents, to the best knowledge of the author, a first attempt to model heavy metal removal in wetland ecosystems, it serves as a record in the identification of a minimum of systems and variables necessary to accurately predict heavy metal uptake by wetland plants.

However, it is abundantly clear in the literature, and the author is well aware, that wetland ecosystems (perhaps more so than other ecosystems) are acutely unique.

While it is believed that the current model is easily applied to other wetland ecosystems in order to predict copper uptake by macrophytic plants, verification of



the model did not occur outside of the Old Woman Creek Wetland study area. This limitation notwithstanding, the results are consistent with the level of copper introduced to the wetland, the productivity of the macrophyte *Nelumbo lutea*, and data for the copper concentration of wetland plants reported throughout the literature.

### 6.3 Future Directions

As stated in the text, data to determine the Michaelis-Menten constants  $V$ ,  $K_M$ , and  $C_{MIN}$  represents a key element in the use of this otherwise simple and applicable equation to the question of heavy metal uptake by macrophytic plants. Wetland-specific research in this regard, for a variety of heavy metals, alone and in combination, is needed if the use of wetlands to treat heavy metal laden wastewater is to achieve widespread use. Utilization of artificial wetlands for municipal wastewater, industrial process water, and stormwater runoff polishing, in addition to other applications, holds great potential as a low-cost, environmentally-friendly treatment technique. The potential growth in the use of harvested wetland biomass as feed, fuel, and fertilizer, is also recognized, and should be explored. However, heavy-metal laden biomass may fall under U.S.E.P.A. hazardous waste regulations, and this needs evaluation.

A greater need in terms of the current modeling effort is the flexibility to model more than one metal, and the need to be able to predict the effect of multiple metals

and complexation agents on the ability of wetland plants to adsorb these constituents. The long-term effects of heavy metal loadings on the viability of the plant itself also requires further study.

Optimum use of artificial wetlands designed for the treatment of wastewater effluents will probably not occur until wetland managers can predict with assurance the effects a particular effluent will have on the wetland fauna and flora. Research or modeling efforts directed at characterizing the effects of particular effluents on artificial wetlands will continue to hold great value.

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